FINAL REPORT

DEVELOPMENT OF ADVANCED HIGH STRENGTH TANTALUM BASE ALLOYS

PART 1 - SCREENING INVESTIGATION

BY

R. W. BUCKMAN, JR.

PREPARED FOR

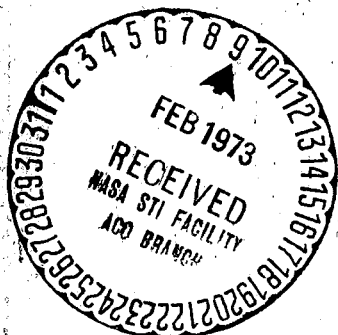NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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MATERIALS AND STRUCTURES DIVISION

Astronuclear Laboratory

Westinghouse Electric Corporation

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FOREWORD

The work described in this report was performed by the Westinghouse Electric Corporation,
Astronuclear Division. Technical administration at the Astronuclear Laboratory was under
the direction of Mr. R. T. Begley while Mr. P. Moorhead served as the NASA Project Manager.
The period covered by the work described was from October 1967 through July 4, 1970.

ABSTRACT

Five experimental tantalum alloy compositions containing 13-18% W+Re+Hf solid solution solute additions with dispersed phase strengthening achieved by carbon or nitrogen additions were prepared as 1.4 inch diameter ingot processed to 3/8 inch diameter rod and evaluated. Elevated temperature tensile and creep strength increased monotonically with increasing solute content. Room temperature elongation decreased from 20% to less than 2% as the solute content was increased above 16%. Phase identification indicated that the precipitating phase in the carbide containing alloys was Ta_2C.

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1.0   SUMMARY OF RESULTS

Five experimental tantalum alloy compositions were prepared as 1.4 inch diameter ingot, processed to rod and evaluated. The ASTAR-811C composition (Ta-8W-1Re-0.7Hf-0.025C) provided the base and strengthening was achieved primarily by increasing the tungsten level with rhenium content restricted from 1-2%. Compositions evaluated were within the range of Ta-13W-1.5Re-0.7Hf-0.025C to Ta-16W-2Re-0.7Hf-0.025C. All five experimental compositions were processed to 3/8 inch diameter rod by a combination of extrusion and swaging at 2550°F using unalloyed molybdenum as a protective cladding.

Tensile and creep strength increased monotonically with increasing tungsten content. The room temperature ductility (28% elongation and 43% R.A.) of the Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1) as recrystallized is similar to that of ASTAR-811C. However, increasing the solute above 16-17% results in a significant decrease in room temperature ductility as evidenced by the 2% elongation and R.A. for the Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) alloy. The stress for 1% elongation is 1000 hours at 2300°F was 24,000 psi for NASVF-1 (13W+1.5Re) and 32,000 psi for NASVF-2 (16W+2Re) compared to 15,000 psi for ASTAR-811C (8W+1Re). Substitution of nitrogen for carbon results in significant improvement in creep properties at 2000°F and below where a nitride bearing composition Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3) had a creep rate at 2000°F and 50,000 psi three orders of magnitude lower than a carbide containing counterpart, Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1). At 2400°F, rapid over-aging of the nitride precipitate resulted in reducing the creep strength below that of the carbide strengthened alloy.

Solution annealing and aging experiments at 1800-2400°F for up to 1000 hours showed that the carbide precipitate Ta_2C undergoes pronounced morphological changes which could not however be related to creep behavior. Further study of this area is required to resolve the role of the carbide in the creep strengthening mechanism. Even though a significant strength advantage over ASTAR-811C was achieved, the Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1) as an electron beam welded joint that had been post weld annealed one hour at 3270°F exhibited bend ductility at room temperature.

The three alloy compositions selected for scale-up as a result of the screening investigation are Ta-14W-1Re-0.7Hf-0.025C, Ta-16W-1Re-0.7Hf-0.025C, and Ta-14W-1.5Re-0.7Hf-0.015C-0.015N. The melting and evaluation of these alloys as two inch diameter ingot will be the topic of a separate report.

2.0   INTRODUCTION

The primary objective of the work described in this report was the development of tantalum base alloy(s) exhibiting higher mechanical strength than ASTAR-811C[1]. ASTAR-811C (Ta-8W-1Re-1Hf-0.025C), developed under contract NAS 3-2542, is a fabricable, weldable sheet alloy which has significantly better creep resistance than any of the commercially available tantalum alloys such as T-111 and Ta-10W[1,2]. The level of strengthening additions to the ASTAR-811C composition was limited by fabricability and weldability considerations. However, it was apparent during this prior investigation that relaxation of the weldability criterion could result in higher elevated temperature strength alloys which would be competitive with the high strength columbium modified TZM molybdenum base alloy. It was with this purpose that development of high strength tantalum base alloys was continued under contract NAS 3-10939. The alloy development was conducted in two sequential phases. During the initial phase, five compositions were selected and prepared as 1.4 inch diameter consumable electrode melted ingots which were processed to 3/8 inch diameter rod for evaluation. The mechanical properties were determined and the results used to select three additional compositions for more detailed evaluation as two inch diameter ingots. This report will describe the results of the Phase I investigation. The five alloy compositions* selected for study during Phase I were:

> Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1)
> Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)
> Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3)
> Ta-16W-1Re-0.7Hf-0.025C (NASVF-4)
> Ta-15W-2Re-0.7Hf-0.025C (NASVF-5)

The hafnium and carbon levels of the above experimental compositions were fixed at that level found to be optimum for ASTAR-811C. Strengthening was then to be achieved primarily by increasing the tungsten content. Minor changes in rhenium content were also investigated

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* All compositions given in weight percent although values for W, Re, and Hf are also essentially same values in atom percent.

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to further define an optimum composition range for this element. Rhenium was shown previously to exert an effect on high temperature creep properties. The upper limit of substitutional solute additions investigated was approximately 19% which would still result in room temperature ductile tantalum alloys as discussed by Buckman and Goodspeed[3]. The substitution of nitrogen for carbon was also investigated since previous work had shown that nitride dispersions were more effective than carbides in improving creep strength below 2400°F[1]. Although nitrogen has a more adverse effect than carbon on the low temperature ductility of tantalum base alloys, particularly as GTA weld bend ductility, relaxation of the latter criterion should permit development of nitride strengthened bar and forging alloys superior to the carbide strengthened counterpart.

3.0   GENERAL EXPERIMENTAL PROCEDURES

3.1   Alloy Consolidation

The experimental alloy compositions were prepared as 1.4 inch diameter x 4 inch long ingot using non-consumable and consumable electrode melting techniques. The second melt electrode, 3/4 inch wide x 24 inch long x 5/8 inch thick bar weighing 1900 grams, was prepared by nonconsumable tungsten electrode d.c. are melting in a water cooled copper trough mold under a 1/3 atmosphere of helium gas. Prior to melting, the chamber was evacuated $<1 \times 10^{-5}$ torr, leak checked and then backfilled with helium gas containing less than 5 ppm total active impurities. To ensure a homogeneous final ingot, the 1900 gram charge was prepared as ten (10) individual 190 gram charges weighed to within 1 mg. The ten charges were then equally spaced along the length of the copper trough and multiple melted. Each bar was melted three times on each side to ensure complete solution of each of the constituents. The trough melted bar was then cast into a 1.4 inch diameter mold by vacuum consumable electrode arc melting using a.c. power. The melt chamber was evacuated to $\leq 5 \times 10^{-6}$ torr prior to arc initiation.

Double electron beam melted Ta-10W and unalloyed W were used as melting stock. Procured as 1/4 inch thick plate, the Ta-10W alloy and unalloyed tantalum were cold rolled to 0.04 inch thick sheet and then sheared to provide chips about 1/16 inch x 1 inch. Tungsten, rhenium and hafnium additions were likewise chipped from 0.02 inch sheet. The highest purity strip commercially available was used for all the alloy additions. Vendor furnished chemical analysis of the starting materials is listed in Table 1. Carbon and nitrogen was added to the alloy charge as -100, +200 mesh tantalum carbide (TaC) and dimetal tantalum nitride (Ta_2N) respectively.

3.2   Primary and Secondary Working

Each ingot was processed to 0.5 inch diameter bar by a combination of extrusion and swaging. The top and bottom of the as-cast ingot were cropped and the side wall conditioned to produce a 1.3 inch diameter x 3-1/2 inch long extrusion billet. The extrusion billet was then

Table 1.   Vendor Analysis of Starting Material

Material	Supplier	Form	Analysis, ppm											
			C	O	N	Cb	Fe	Si	Mo	Zr	Ti	Hf	Re	W
Tantalum	Wah Chang	Plate	<30	<50	26	412	<15	<20	<10	70	11	--	--	385
Ta-10W	Fansteel	Plate	10	10	10	<500	40	<10	150	--	<10	--	--	9.95%
Hafnium	Carborundum	Strip	80	100	16	--	40	--	--	2.1%	--	--	--	--
Tungsten	Fansteel	Strip	--	--	--	--	--	--	--	--	--	--	--	99.95%
Rhenium	Chase-Brass	Strip	--	--	--	--	--	--	--	--	--	--	*99.99%	--

* Specification minimum

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encapsulated in a 1.8 inch diameter arc cast molybdenum cladding which was sealed by electron beam welding. The molybdenum clad billet was then heated by induction under a flowing argon cover gas to $2550^{\circ}F$. After soaking at $2550^{\circ}F$ for 10 minutes, the heated billet was transferred to the container of a model 1220C Dynapak (HERF) and then extruded to round bar through a zirconia coated die with a 0.940 inch diameter opening.

The molybdenum clad extrusion was cropped to remove the nose and tail sections and after chemically cleaning, recrystallized by heating for 1 hour at $3000^{\circ}F$ at 1×10^{-5} torr. The annealed molybdenum clad bar was first heated above $1800^{\circ}F$ in an argon purged retort. At this temperature, the solubility of hydrogen in tantalum is <30 ppm. The heated bar was then transferred to the hydrogen atmosphere furnace which was at $2500^{\circ}F$ and swaging to final diameter of 0.4 inch was accomplished in 10-15% reduction per pass. The temperature of the bar was never allowed to cool below $1800^{\circ}F$ and was reheated to $2500^{\circ}F$ between each pass. Swaging was continued until the diameter of the tantalum alloy wore was reduced to 0.4 inches. Following swaging, the molybdenum cladding was chemically removed and the as-swaged bar was sectioned for mechanical property evaluation and recrystallization studies.

3.3   Mechanical Property Testing

Shoulder loaded round bar test specimens with a 0.1 inch uniform diameter gage length of one inch were used for the mechanical property evaluations. Short time tensile properties were determined at a constant strain rate of 0.05 in/minute. Elevated temperature tensile testing was done at $\leq 1 \times 10^{-5}$ torr in a self resistance heated split tungsten element cold wall vacuum furnace. All creep testing was done at $\leq 1 \times 10^{-8}$ torr in sputter ion pumped units of the type described by Buckman and Hetherington[4].

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3.4 Heat Treatment

All heat treatments were performed in cold wall tantalum resistance heated vacuum furnaces at pressures of $\leq 1 \times 10^{-5}$ torr. Prior to annealing all specimens were pickled in a solution of equal parts of H_2O-HF-HNO_3 to ensure removal of any contaminated layers. All annealing specimens were then wrapped with 0.002 inch thick chemically cleaned tantalum foil to further minimize any possibility of contamination.

4.0   EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1   Melting

All five experimental compositions were satisfactorily consolidated as 1.4 inch diameter ingot. A typical example of a trough melted bar and an as–melted ingot are shown in Figure 1. Samples taken from the bottom portion of each ingot were chemically analyzed for the intentional alloy additions and the results are listed in Table 2. Excellent recovery of the alloy additions was demonstrated and all compositions were as intended with the exception of the hafnium in NASVF–4 and 5 where it appears that double the amount was inadvertently added.

4.2   As–Cast Microstructures

Typically the as–cast microstructure of the carbide containing alloy was two phase, containing a carbide precipitate (Ta_2C) in a solid solution strengthened matrix (See Figure 2a). This microstructure is very similar to that exhibited by as–cast ASTAR–811C[1]. Dendritic freezing gave rise to a rather pronounced cored microstructure in the as–cast ingot as illustrated in the low magnification photomicrograph in Figure 2b. The room temperature hardness of the as–cast carbon containing alloy compositions varied linearly as a function of the alloy content as illustrated in Figure 3. The nitrogen bearing compositions Ta–13W–1.5Re–0.7Hf–0.03N (NASVF–3) has a significantly higher hardness than the carbon containing counterpart Ta–13W–1.5Re–0.7Hf–0.025C (NASVF–1), 417DPH, vs. 345DPH, and reflects the apparent higher solubility of nitrogen in the alloy matrix. The microstructure of the as cast nitrogen bearing composition appeared single phase when viewed optically at a magnification of 1500X.

4.3   Primary Working

All of the experimental tantalum alloy compositions extruded satisfactorily. The molybdenum cladding remained intact and there were no evidence of extrusion defects. A typical conditioned billet and molybdenum clad components are shown in Figure 4a while the

Figure 1. Trough Melted, Second Melt Electrode and 1.4 Inch Diameter As-Cast Ingot

Table 2. Composition of Consumable Electrode Melted 1.4 inch Diameter Ingots

Nominal Composition, Weight % (Ident. No.)	Analyzed Content, Weight %				
	W	Re	Hf	C	N
Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1)	12.9	1.6	0.68	0.024	0.0018
Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)	16.2	2.1	0.65	0.024	0.0021
Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3)	14.1	1.5	0.59	---	0.032
Ta-16W-1Re-0.7Hf-0.025C (NASVF-4)	15.5	0.98	1.4	0.032	---
Ta-15W-2Re-0.7Hf-0.025C (NASVF-5)	14.5	2.2	1.1	0.028	---

* All samples taken from bottom portion of ingot.

a) Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1)

1500X

b) Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)

100X

Figure 2. Typical As-Cast Microstructure of Carbide Containing
Experimental Tantalum Alloy Compositions

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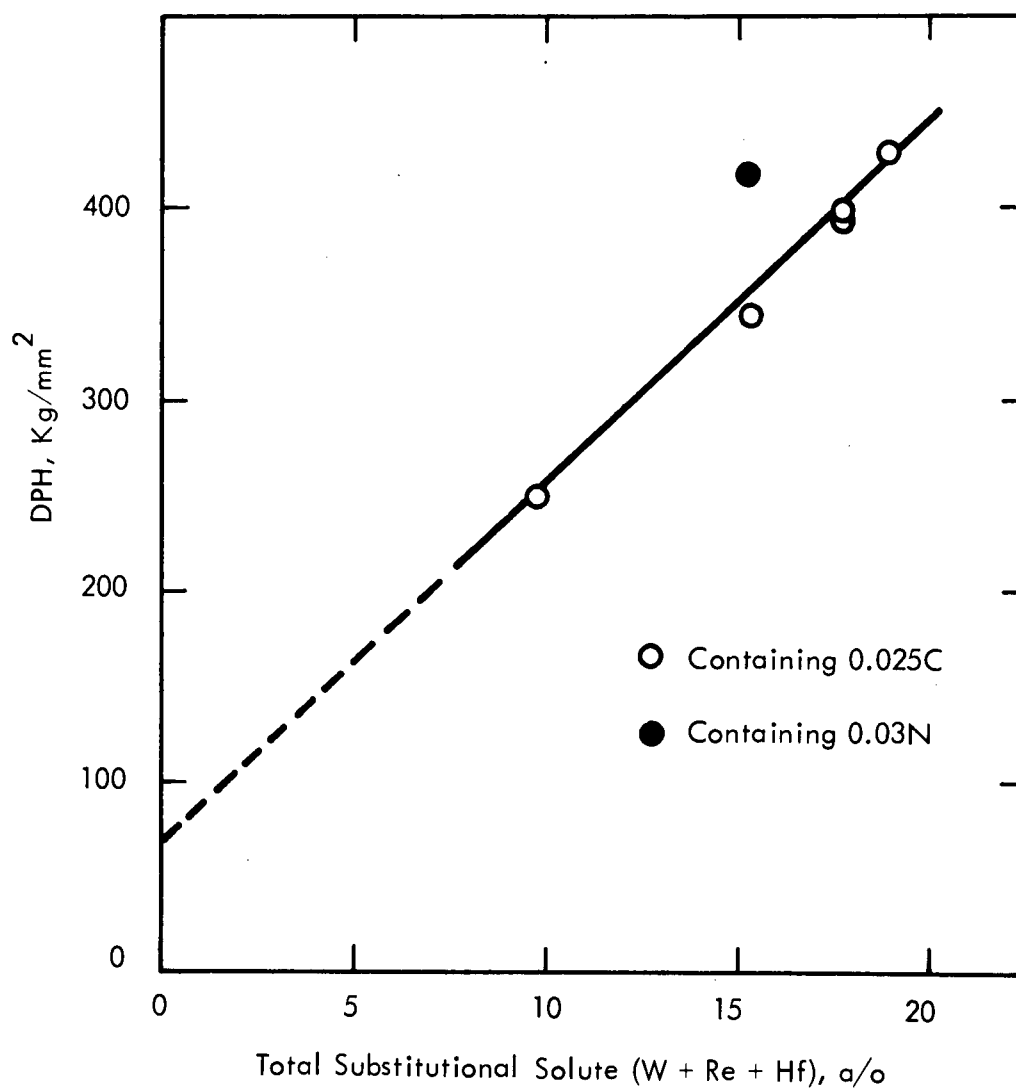
Figure 3. Effect of Solute Content (W + Re + Hf) on the Room Temperature
Hardness of As Cast Tantalum Base Alloys

Molybdenum Can

Tantalum Alloy Billet

Westinghouse Astronuclear Laboratory

Molybdenum Tail Plug

a) Extrusion Billet and Cladding

Westinghouse Astronuclear Laboratory
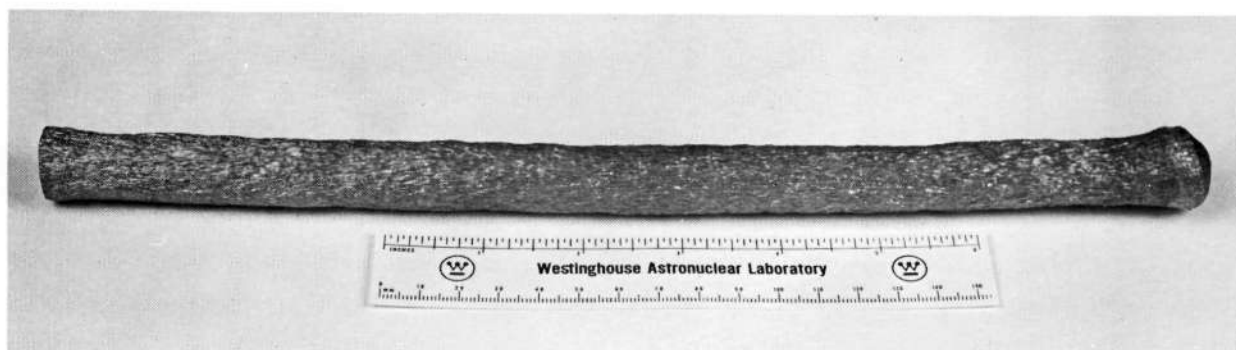
b) Declad Tantalum Alloy Extrusion

Figure 4. Tantalum Alloy Extrusion Billet, Molybdenum Cladding
and Resultant Extrusion with Cladding Removed

declad extrusion in Figure 4b illustrates the soundness and uniformity of the extrusion core.
All the billets were extruded in the as-cast condition. Since nitrogen bearing tantalum alloy
compositions have been shown to be responsive to thermal treatment,[1] samples of as-cast
NASVF-3 were annealed for 2 and 16 hours at 2370°F and 2550°F in an attempt to reduce the
as-cast hardness by overaging the nitride precipitate. The as-cast hardness of 417DPH was
only reduced to 406DPH after each of the heat treatments, thus NASVF-3 was extruded in
the as-cast condition.

The reduction by extrusion was 4:1 and was accomplished at 2550°F which is approximately
0.5T$_m$ of the alloys. In all cases, the as-extruded microstructure was typical of a worked
material, i.e. elongated grains parallel to the working direction, (See Figure 5a). However,
the room temperature hardness of the as-extruded material was only ≤10% of the starting
hardness (See Table 3). This would tend to indicate that a significant amount of recovery
occurred during and after extrusion. One hour at 3000°F was sufficient to cause recrystalliza-
tion of the as-extruded microstructure as shown in Figure 5b.

The primary purpose of the primary hot working operation is to promote homogenization of the
cored as-cast microstructure. Examination of samples from the tail end of the Ta-16W-2Re-
0.7Hf-0.025C revealed evidence of the as-cast microstructure in the as-extruded condition
(Figure 6a) and after recrystallizing 1/2 hour at 3000°F (Figure 6c), one interesting feature
noted upon examination at 1500X was the presence of a discontinuous precipitate (Figure 6b)
in the as-extruded microstructures. This was not observed in the as-cast samples examined,
thus it may be assumed that it formed during the extrusion operation. During the subsequent
recrystallization anneal, the lamellar precipitate appears to be breaking down (Figure 6d).
Discontinuous precipitation has been observed in the base metal and weldments of ASTAR-811C[5]
subjected to extended aging times. Evidence of this precipitate was not observed during the
initial development work in ASTAR-811C[1] and when observed for these alloy compositions, it
was at first thought caused by the higher tungsten content. However, this has been shown not

Table 3. Room Temperature Hardness of Experimental Tantalum
Alloys in the As-Extended and Annealed Condition

| Composition/Ident. No. | DPH, Kg/mm^2 | | | | |
	As Cast	As-Extruded		Annealed 1 hour at 3000°F	
		Nose	Tail	Nose	Tail
Ta-13W-1.5Re-0.7Hf-0.025C/NASVF-1	345	401	390	346	342
Ta-16W-2Re-0.7Hf-0.025C/NASVF-2	427	---	433	---	398
Ta-13W-1.5Re-0.7Hf-0.03N/NASVF-3	417	446	414	410	387
Ta-16W-1Re-0.7Hf-0.025C/NASVF-4	393	421	418	393	374
Ta-15W-2Re-0.7Hf-0.025C/NASVF-5	397	431	419	395	377
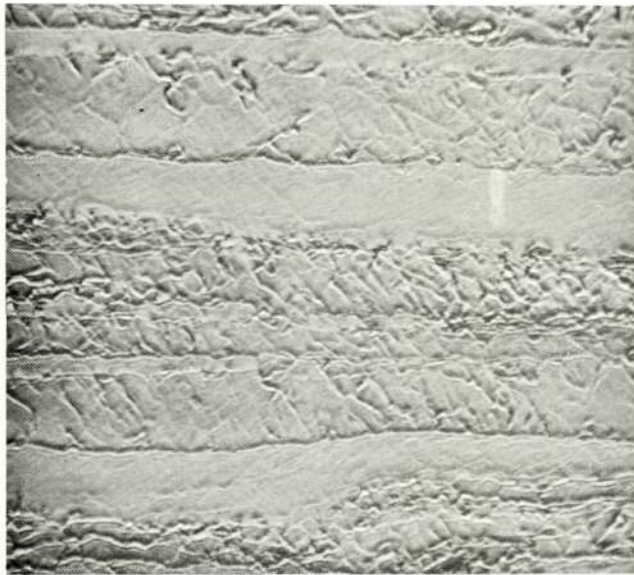
a) As Extruded   390DPH

b) a + 1 hour at 3000°F   342DPH

Figure 5. Microstructure of Ta–13W–1.5Re–0.7Hf–0.025C (NASVF–1)
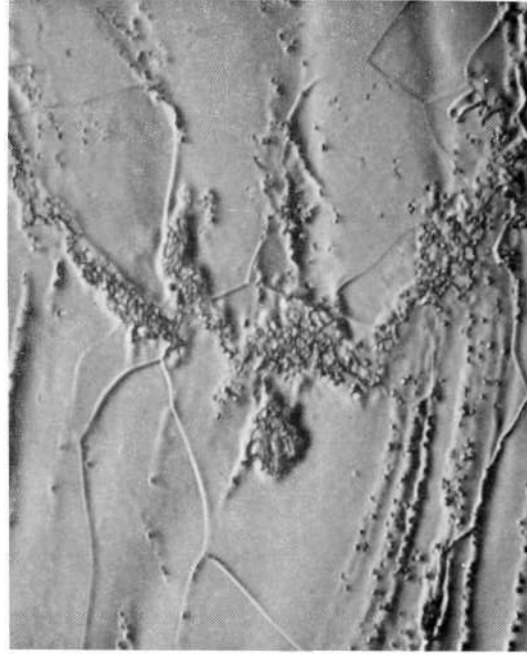Mag. 1500X

b) As Extruded 1500X

d) (a) + 1/2 hour at 3000F 1500X

a) As Extruded 100X
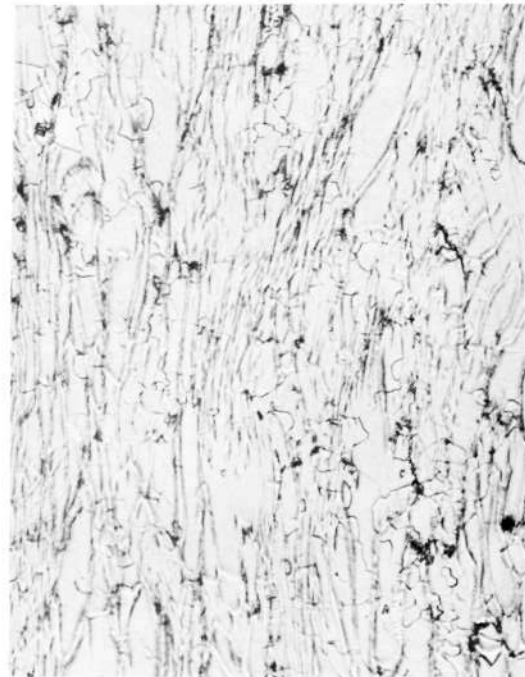
c) (a) + 1/2 hour at 3000F 100X

Figure 6. Microstructure of Ta–16W–2Re–0.7Hf–0.025C (NASVF–2)

to be the case as illustrated in more detailed examination of ASTAR-811C.[5] The sequence of events which lead to the discontinuous precipitate are not well understood.

4.4 Secondary Working and Recrystallization Behavior

The as-extruded bar was recrystallized with the molybdenum clad intact and then was hot swaged to final size. As extruded, the alloy core diameter eas approximately .7 inch and the final as-swaged diameter was .44 inches, a reduction in area of nominally 60-65%. The bars were heated to 2500°F for swaging, and reductions of 10% per pass were taken until the final diameter was reached. Between each pass, the bar was reheated to 2550°F. Heating for swaging was accomplished in a hydrogen atmosphere furnace. Prior to insertion into the hydrogen atmosphere furnace, the bars were heated to 1800°F in an argon atmosphere furnace. This procedure did not result in any adverse effects on the workability as all five compositions were satisfactorily worked to the required final diameter.

As swaged, the microstructure was typical of a worked microstructure. Formation of equiaxed grains occurred in the carbide containing compositions after heating for one hour at 2900 – 3100°F. The one hour recrystallization behavior of the experimental tantalum alloy is summarized in Table 4 and illustrated in Figure 7. Also included in Figure 7 for comparative purposes in the recrystallization curve for ASTAR-811C. Since the high strength tantalum alloy compositions were hot worked, significant recovery occurred during the working operations and interpass annealing operations and is reflected by the modest change to the as-swaged hardness as the annealing temperature is increased. In contrast, the curve for the cold worked ASTAR-811C shows a significant reduction in as-worked hardness as the annealing temperature is increased. The variations in the shape of the isochronal curve for the carbide containing compositions most probably reflects uncontrolled differences in cooling rates from the annealing temperature and this would affect the amount of carbon retained in solution. Carbide solutioning for the experimental compositions occurred at 3630°F and is similar to that for ASTAR-811C. The hot swaging and recrystallization anneal was sufficient to

Table 4. Recrystallization Behavior of Experimental Tantalum Alloy Rod

Composition, W/O	As-Swaged***	Hardness (DPH)* and Microstructure** after annealing one hour at (°C/°F).								
		1000/1830	1200/2190	1300/2370	1400/2550	1500/2730	1600/2910	1700/3090	1800/3270	2000/3630
Ta-13W-1.5Re-0.7Hf-0.025C	416 W	375 W	356 W	353 W	348 W	353 W	348 W	--- ---	346 R	359 R
Ta-16W-2Re-0.7Hf-0.025C	439 W	426 W	401 W	--- ---	381 W	--- ---	375 R	408 R	410 R	404 R
Ta-13W-1.5Re-0.7Hf-0.03N	434 W	417 W	410 W	--- ---	394 W	--- ---	409 W	--- ---	399 R	382 R
Ta-16W-1Re-0.7Hf-0.025C	414 W	402 W	367 W	--- ---	358 W	359 R_P	369 R_X	402 R_X	420 R_X	439 R_X
Ta-15W-2Re-0.7Hf-0.025C	422 W	408 W	365 W	--- ---	363 W	362 R_P	379 R_X	421 R_X	421 R_X	431 R_X

*30K$_g$ load, avg. of 5 impressions

**W = Wrought
R_P = <25% Equiaxed grains
R_X = >99% Equiaxed grains

***Reduced 60-65% subsequent to the last recrystallization anneal. Material heated at 2550°F for swaging.
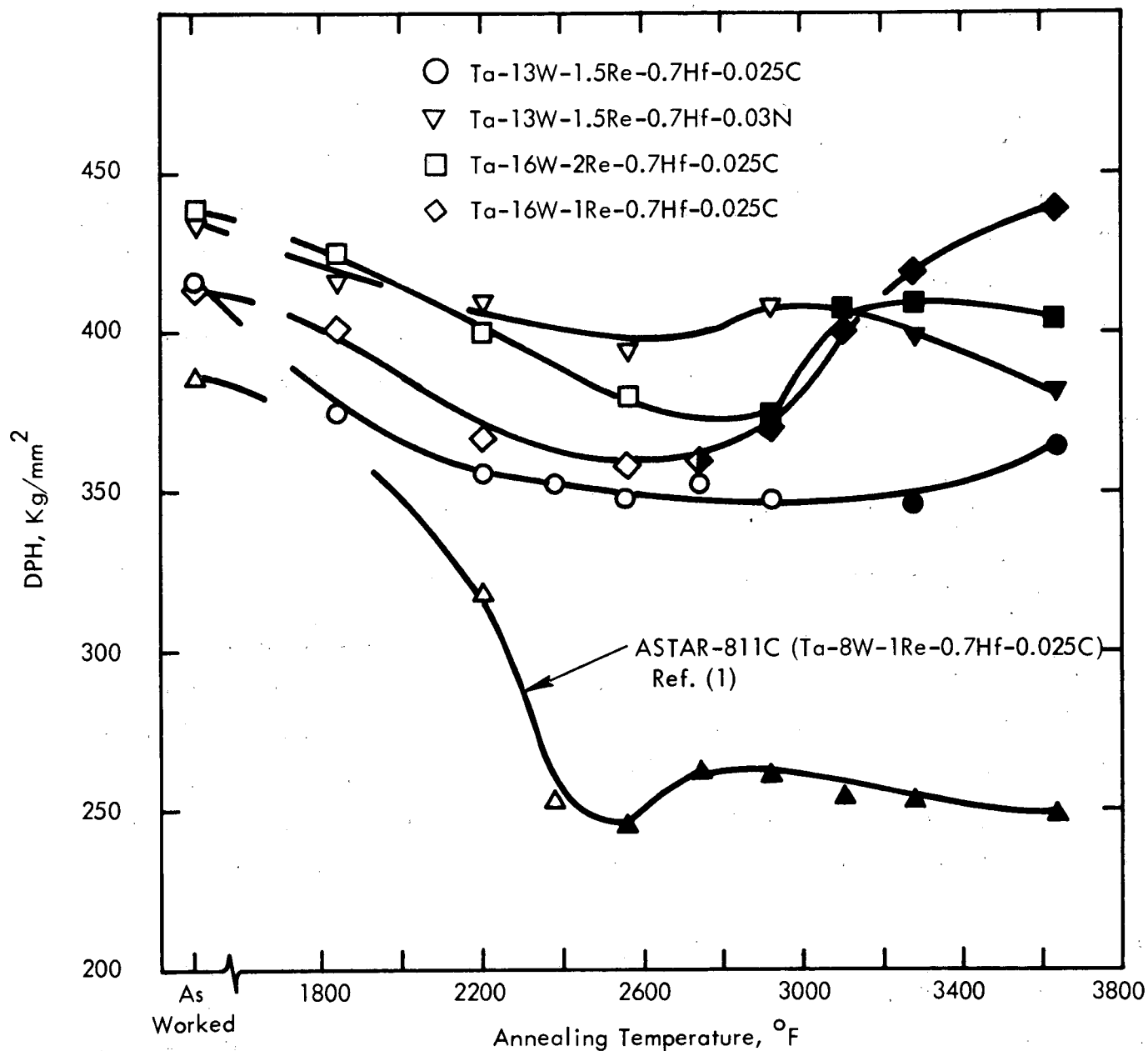
Figure 7. Recrystallization Behavior of As Swaged (60–65%) Tantalum Alloy Rod
{ open symbols – wrought microstructure
partially closed symbols – partially equiaxed microstructure
closed symbol – 100% equiaxed microstructure }

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remove all evidence of the prior as-cast structure that persisted in the extrusion of the Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) composition (See Figure 8 and Figure 6).

The recrystallization behavior of the nitrogen bearing composition, Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3) did not differ significantly from its carbon containing counterpart (See Table 4 and Figure 7). The only exception was of course that the hardness level of NASVF-3 remained about 50DPH units higher than NASVF-1. As swaged, the microstructure of NASVF-3 was two phase and a fine nitride precipitate was observed. After annealing at 3630°F, the nitride precipitate was returned to solid solution and was not observed when viewed at 1500X magnification (See Figure 9). The isolated precipitates seen in Figure 9b are most probably oxides.

4.5   Mechanical Properties

4.5.1 Tensile Properties

Tensile properties were determined at room temperature, 2000, and 2400°F for each of the experimental compositions. Prior to testing, each specimen was annealed for one hour at 3300°F. This final annealing temperature was selected since results of the recrystallization study on the as-swaged rod had indicated that this treatment produced a uniform recrystallized grain size of 0.04 mm. Annealing for one hour at 3000°F did not always result in a completely equiaxed microstructure and annealing at 3600°F resulted in a large grain size (0.09 mm).

The tensile data for the advanced tantalum alloy compositions are summarized in Table 5. Tensile yield strength at R.T., 2000, and 2400°F and room temperature elongation are plotted as a function of total solute content in Figure 10. It is apparent from this plot, that increasing the substitutional solute content of a Ta-0.025C matrix above 16-17% results in a decrease in the room temperature ductility. Although the elevated temperature strength is increasing monotonically with increasing solute content, a trade off in elevated temperature strength must be made in order to retain room temperature ductility since low temperature ductility is a prime feature of tantalum base alloys.

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a) As Swaged

b) 1 Hour at 2550°F
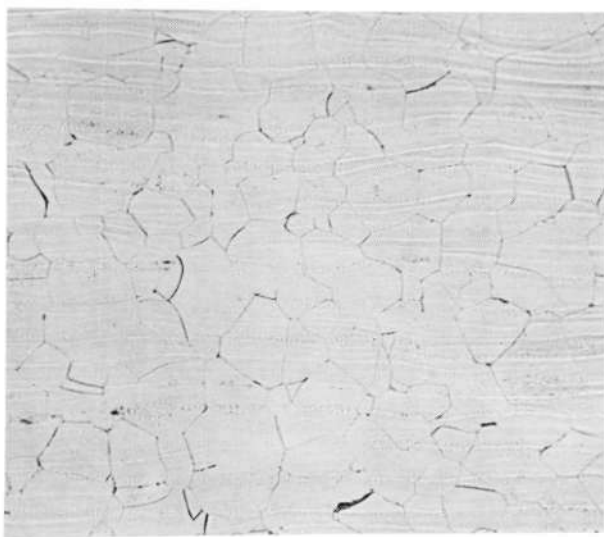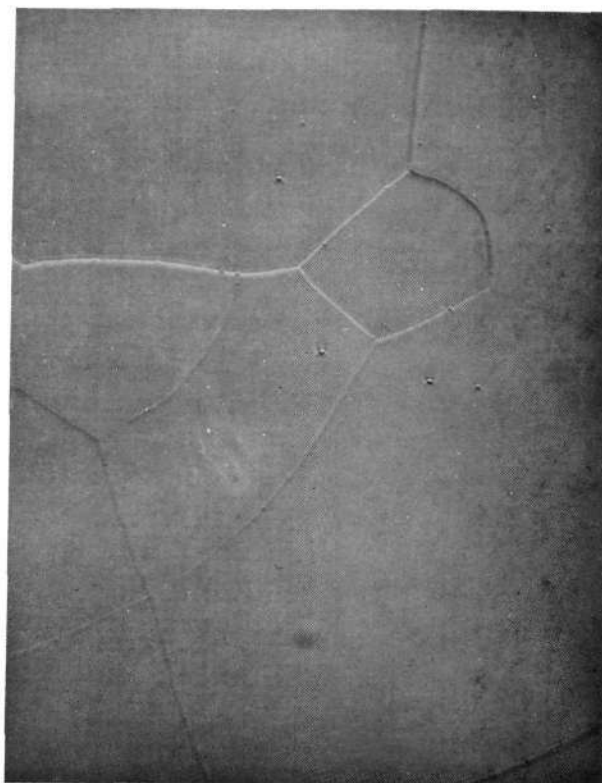
c) 1 Hour at 3270°F

d) 1 Hour at 3630°F

Figure 8. As–Swaged and Annealed Microstructures of
Ta–16W–2Re–0.7Hf–0.025C Rod. Mag. 200X

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a) As Swaged

b) 1 Hour at 3630°F

Figure 9. Microstructure of Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3)
Rod in the As-Swaged and Solution Annealed Condition
1500X

Table 5. Tensile Properties of Experimental Tantalum Base Alloys

Composition/Heat No.	Test Temp. °F	0.2% Offset Yield Strength (psi)	Ultimate Tensile Strength (psi)	% Elongation Uniform (%)	% Elongation Total (%)	Reduction in Area (%)	Modulus of Elasticity (psi × 10⁻⁶)
Ta–13W–1.5Re–0.7Hf –0.025C/NASVF–1	R.T.	119,200/118,600(a)	139,900	14.3	27	43.5	33.9
	2400	44,000	58,300	9.5	30	55.9	---
Ta–16W–2Re–0.7Hf –0.025C/NASVF–2	R.T.	170,000	172,000	1.8	1.8	2.0	---
	2000	72,730	115,600(b)	8.7	8.7(b)	8.7(b)	---
	2400	49,500	65,600	10.0	31.5	46.8	---
Ta–13W–1.5Re–0.7Hf –0.03N/NASVF–3	R.T.	160,100	166,000	15.7	15.7	16.0	---
	2000	61,000	92,300	11.3	14.0	27.0	---
	2400	49,600	72,400	6.7	7.3	12.9	---
Ta–16W–1Re–1.4Hf –0.025C/NASVF–4	R.T.	167,000	167,000	8.0	8.0	8.0	30.1
	2000	76,800	119,700	16.6	20.4	57.7	---
	2400	56,620	80,470	11.0	20.8	58.5	---
Ta–15W–2Re–1.1Hf –0.025C/NASVF–5	R.T.	168,000	168,000	4.6	4.6	4.6	31.9
	2000	64,500	118,500	20.3	24.9	60.0	---
	24000	(c)	71,280	18.0	23.0	52.8	---

(a) Upper/lower yield points

(b) Reached load limit of tensile machine—test stopped prior to fracture

(c) Cam stuck on chart drive – specimen loaded past yield point

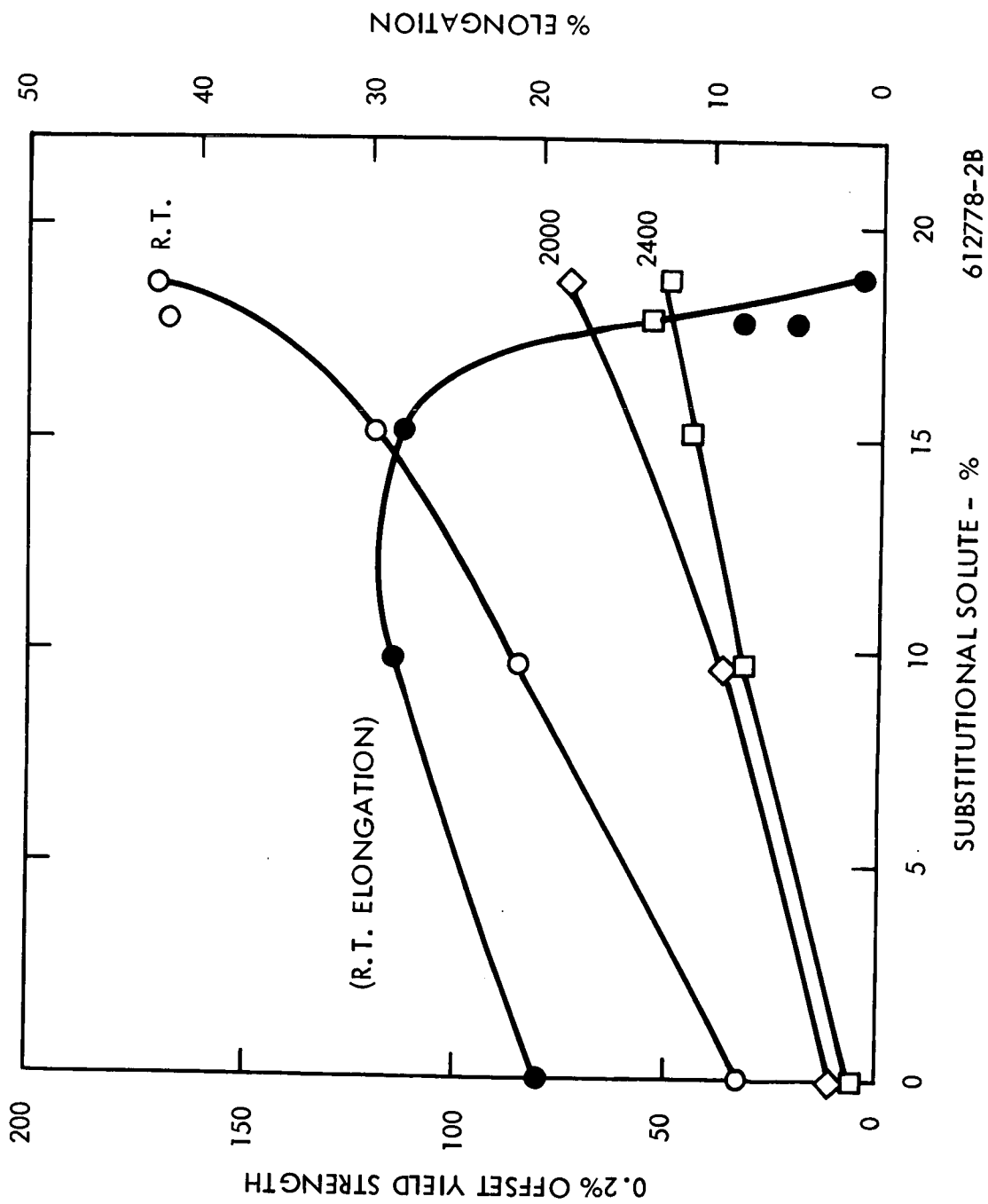. All specimens annealed 1 hour at 3300°F prior to test at constant speed of 0.05 in/min

Figure 10. Effect of Substitutional Solute Level on Yield Strength and Room Temperature Elongation of Ta-8-16W-1-2Re-0.7Hf-0.025C Alloy Rod (Annealed 1 Hour at 3300°F Prior to Test)

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Substitution of carbon in the Ta-13W-1.5Re-0.7Hf-0.25C (NASVF-1) with an equivalent amount of nitrogen results in a significant strength increase at room temperature but only a minor improvement at elevated temperature (See Figure 11). The most noticeable effect was on elongation where the nitrogen bearing composition exhibited significantly lower tensile ductility over the entire test temperature range.

4.5.2 Creep Properties

The limited amount of material processed for each composition allowed only two creep specimens per alloy. Thus stress change creep testing was utilized to maximize the characterization of the time dependent deformation. The creep behavior of the experimental tantalum alloy compositions is summarized in Table 6 and the data are plotted in Figure 12. Prior to creep testing, specimens were annealed either at 1800°C or 2000°C. As noted earlier, formation of a completely equiaxed microstructure was not generally observed until after a one hour anneal at 1800°C. During the development of A-811C, annealing at 2000°C gave a significant improvement in creep behavior.

The creep rate of the carbide strengthened experimental compositions did not appear to significantly differ whether the final annealing treatment was at 1800°C or 2000°C. For example, the Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1) after annealing 1 hour at 1800°C and tested at 50,000 psi and 1850°F resulted in a creep rate of 0.00 1%/hour. The specimen was removed from the test unit and then reannealed for one hour at 2000°C and then retested at 1850°F and 50,000 psi. The secondary creep rate ($\dot{\epsilon}_s$) was 0.00065%/hour which is not significantly different for that exhibited by the 1800°C annealed specimen.

The Larson-Miller representation of the data in Figure 12 was plotted using time to elongate 1% as the time parameter, and this was calculated from the steady state creep rate. For a given stress there was generally a significant spread in the values of Larson-Miller parameter as the temperature was varied thus indicating a change in the rate controlling mechanism. Values for activation energy were calculated from the temperature change data and the
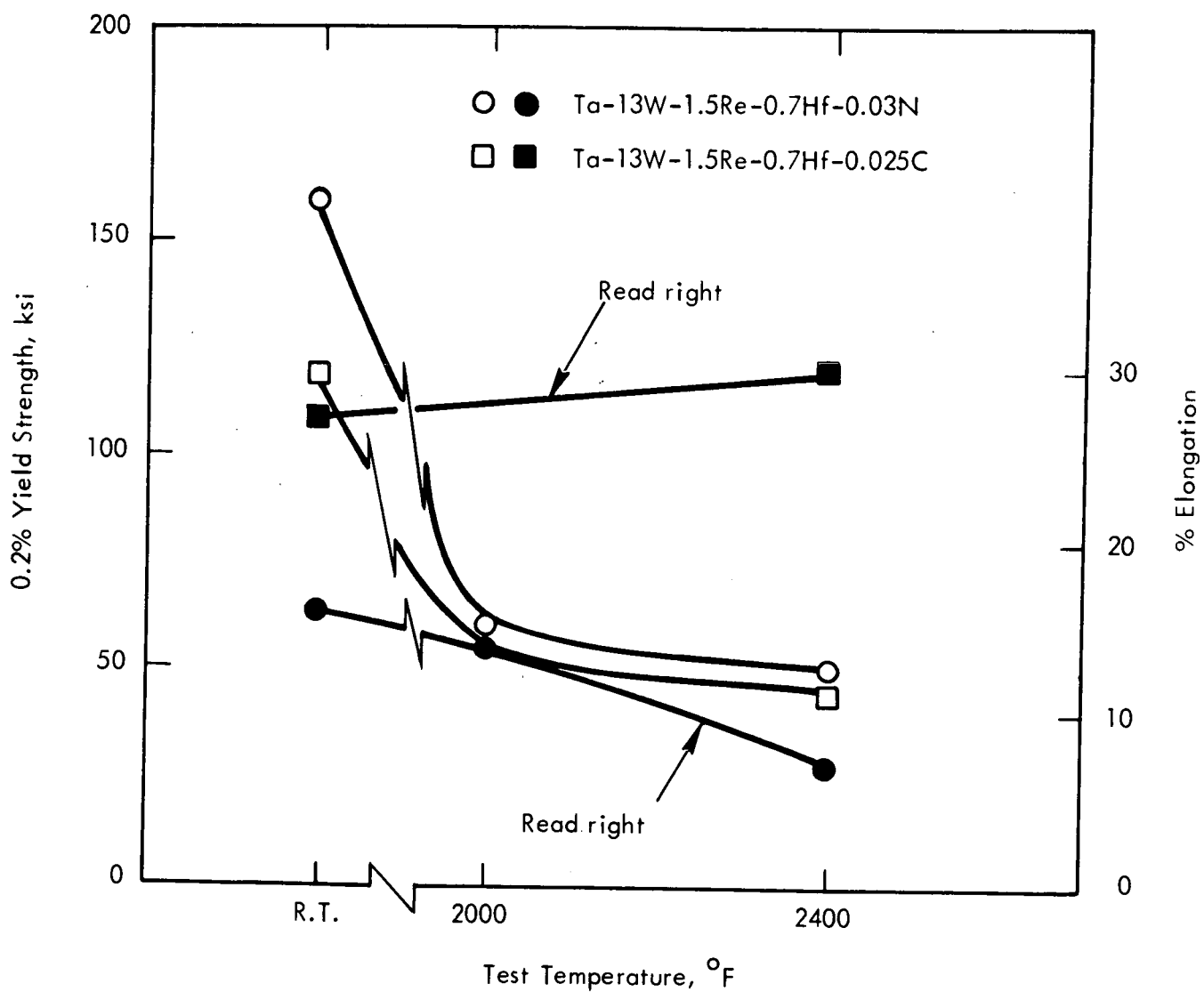
Figure 11. Effect of Nitrogen Substitution for Carbon on Strength and Ductility of Ta-13W-1.5Re-0.7Hf-0.025C Alloy

Table 6. Creep Behavior of Experimental Tantalum Base Alloys (Swaged Bar)

Composition (Heat No.)	Specimen Identification	Test[a] Temperature (°F)	Applied Stress (psi)	Test Time (hrs)(e)	Total Elongation (%)	Secondary Creep Rate %/hr	Time to 1% Elong. (hrs)	Larson-Miller Parameter P × 10³
Ta-13W-1.5Re -0.7Hf-0.025C (NASVF-1)	-1C[b]	2000	50,000	25	2.41	0.078	13	37.2
		1900	50,000	354	3.20	0.0009	1110	42.6
		1850	50,000	498	3.	0.0010	965	41.5
	-1B[b]	2400	30,000	25	0.54	0.0195	52	47.0
		2300	30,000	167	1.26	0.0053	187	47.6
		2250	30,000	331	1.60	0.0026	385	47.6
		2300	30,000	500	2.68	0.0056	178	47.6
	-1C[c]	1850	50,000	430	1.16	0.00065	1540	42.0
Ta-16W-2Re -0.7Hf-0.025C (NASVF-2)	-2D[c]	1850	50,000	160	0.12	(f)	---	---
		1900	50,000	304	0.15	(f)	---	---
		1950	50,000	474	0.53	0.000625	1600	43.8
		2000	50,000	702	0.87	0.000745	1340	44.6
		2050	50,000	1023	1.34	0.00121	825	45.0
	-2E[c]	2400	30,000	363	0.92	0.0026	384	50.3
		2350	30,000	764	1.80	0.0022	450	49.7
		2300	30,000	979	2.03	0.00107	935	49.7
Ta-13W-1.5Re -0.7Hf-0.03N (NASVF-3)	-3D[b]	1850	50,000	500	0.15	0.0	---	---
		1900	50,000	980	0.28	0.0	---	---
		1950	50,000	1200	0.35	0.000138	7250	45.4
		2000	50,000	1492	0.48	0.000213	4600	45.9
	-3E[b]	2400	30,000	290	1.22	0.000541	1848	52.2
		2300	30,000	460	2.51	0.0102	98	46.9
		2250	30,000	625	3.72	0.0071	141	46.4

Table 6. Creep Behavior of Experimental Tantalum Base Alloys (Swaged Bar) (continued)

Composition (Heat No.)	Specimen Identification	Test[a] Temperature (°F)	Applied Stress (psi)	Test Time (hrs)[e]	Total Elongation (%)	Secondary Creep Rate %/hr	Time to 1% Elong. (hrs)	Larson-Miller Parameter P × 10³
Ta-16W-1Re -1.4Hf-0.025C (NASVF-4)	-4D[c]	1850	50,000	310	0.2	0.00032	3130	42.7
		2000	50,000	480	1.0	0.00385	260	42.8
		2100	50,000	500	1.74	0.035	29	42.2
		2200	50,000	505	2.50	0.167	6	42.0
		2100	50,000	522	3.20	0.0425	24	41.9
		2000	50,000	545(g)	3.45	0.0104	97	39.3
	-4E[c]	2400	30,000	222	1.04	(R)	215	49.5
		2300	30,000	507	1.44	0.00114	890	49.5
Ta-15W-2Re -1.1Hf-0.025C (NASVF-5)	-5D[c]	1850	50,000	240	0.3	0.00047	2170	42.4
		2000	50,000	308	1.12	0.00633	158	42.3
		2100	50,000	312	1.70	0.081	12	41.3
		2200	50,000	313	2.64	0.9	1	40.0
		2000	50,000	438	3.04	0.00387	258	42.7
	-5E[c]	2400	30,000	402	1.57	(R)	326	50.1
		2200	30,000	646	1.55	0.000235	4250	49.5
		2400	30,000	708	2.17	0.0108	92	48.5
		2500	30,000	732	3.50	0.0523	19	48.3
		2600	30,000	735	4.8	0.298	3	47.6
		2500	30,000	743	5.5	0.08	12	47.5
Ta-8W-1Re -0.7Hf-0.025C (NASV-20) ASTAR-811C	-20R1[k]	2000	30,000	450	1.08	0.00128	781	44.0
		2100	30,000	532	2.00	0.0125	80	43.3
		2000	30,000	890	2.50	0.00148	675	43.8

Table 6. Creep Behavior of Experimental Tantalum Base Alloys (Swaged Bar) (continued)

Notes:

(a) Temperature change creep test

(b) Annealed 1 hour at 1800°C (3270°F)

(c) Annealed 1 hour at 2000°C (3630°F)

(d) Calculated from $\dot{\epsilon}_s$ (secondary creep rate)

(e) Represents total accumulated test time

(f) Insufficient change in strain to determine reliable creep rate

(g) Specimen fractured at 550 hours

(h) Creep curve did not exhibit $\dot{\epsilon}_s$

(k) 3/8 diameter bar, swaged at room temperature ($\sim$60% reduction) plus annealed 1/2 hour at 3600°F

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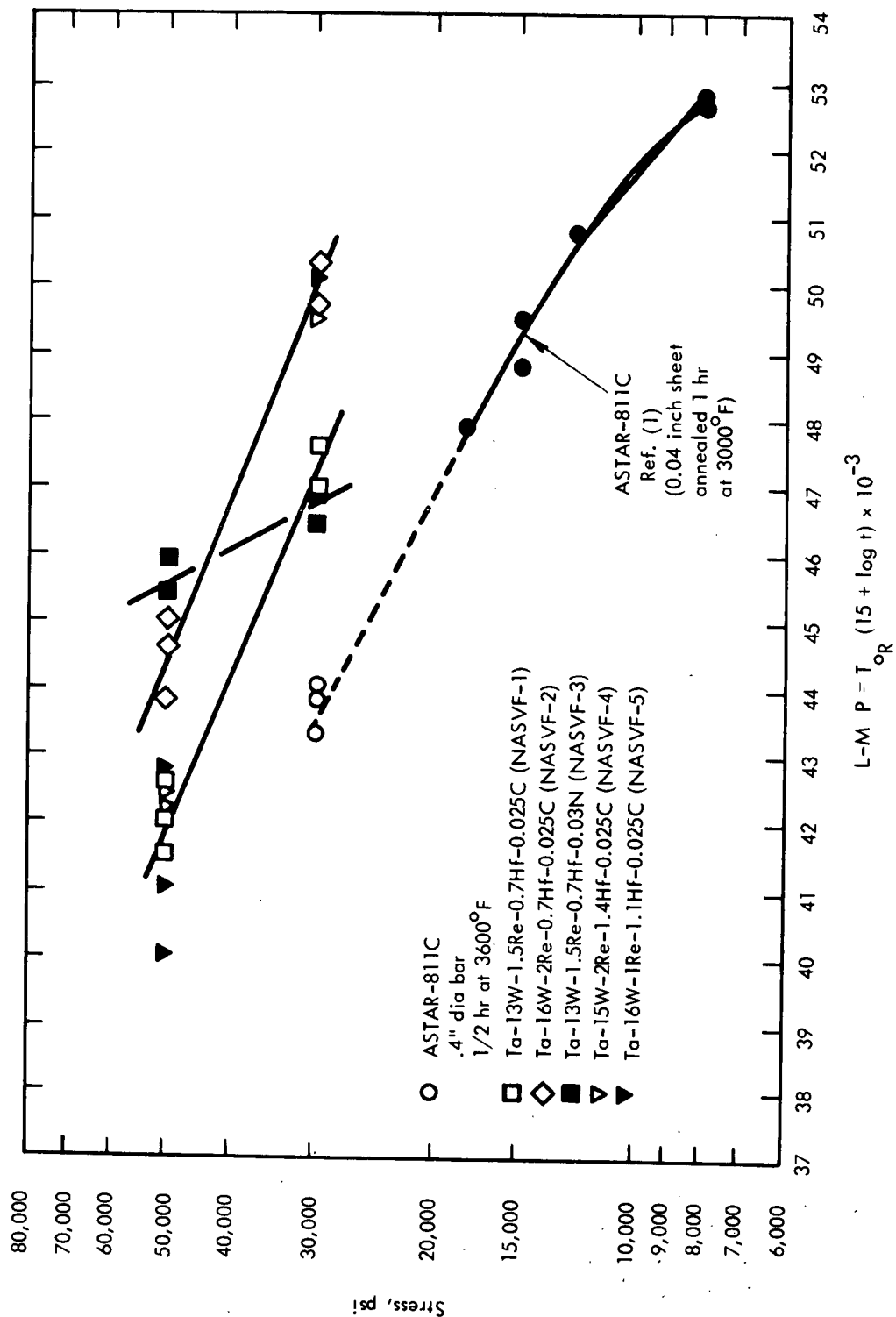
Figure 12. Creep Properties of Experimental Tantalum Base Alloys

$$\text{L-M } P = T_{o_R} \; (15 + \log t) \times 10^{-3}$$

where t = time to elongate 1% in hours

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values ranged from 25 to 192 kcal/mole. The activation energy for self diffusion for tantalum is accepted as 110 kcal/mole.[6] Generally the segments of the creep curves at the various temperature levels after the initial condition were linear. However, it is difficult to ascribe physical processes to each of the values of activation energies calculated and may reflect more the limit to which the data may be interpreted. At 1850-2000°F, protracted transient creep was observed (See Figure 13), while at 2400°F, the typical concave upward creep curve was seen. From Figure 12, it is apparent that the advanced tantalum base alloys are significantly superior to A-811C as far as creep properties are concerned. All of the creep data for A-811C was determined on sheet. ASTAR-811C 3/8 inch diameter swaged rod was annealed for one-half hour at 3600°F and tested at 30,000 psi at 2000°F and 2100°F. The resultant creep curve is shown in Figure 14. The primary creep stage existed for approximately two hundred hours after which the rate was linear. Increasing the temperature resulted in an order of magnitude increase in creep rate. The creep rate was linear for the eighty hours at 2100°F. Although not shown in Figure 14, the temperature was reduced to 2000°F and linear creep was observed for approximately 400 hours at which time the test was terminated. Initially at 2000°F, the $\dot{\epsilon}_s$ was 0.00125%/hour and after increasing to 2100°F and return to 2000°F, the $\dot{\epsilon}_s$ was 0.00148%/hour and is essentially unchanged over the original thus indicating little influence of the exposure at 2100°F. The creep rate data were used to calculate values for L-M parameter and are included in Figure 12. Extrapolation of the ASTAR-811C sheet data coincides with the round bar data indicating little influence of working history.

Creep strength of the carbide strengthened alloy compositions increased monotonically with solute content as illustrated in Figure 15. However, as noted earlier, there is a significant decrease in room temperature ductility as the solute content exceeds approximately 16% W+Re.

Previous work had shown that rhenium had a potent effect on the creep behavior of tantalum base alloys. Compositions NASVF-4 and NASVF-5 were identical and each contained 17%
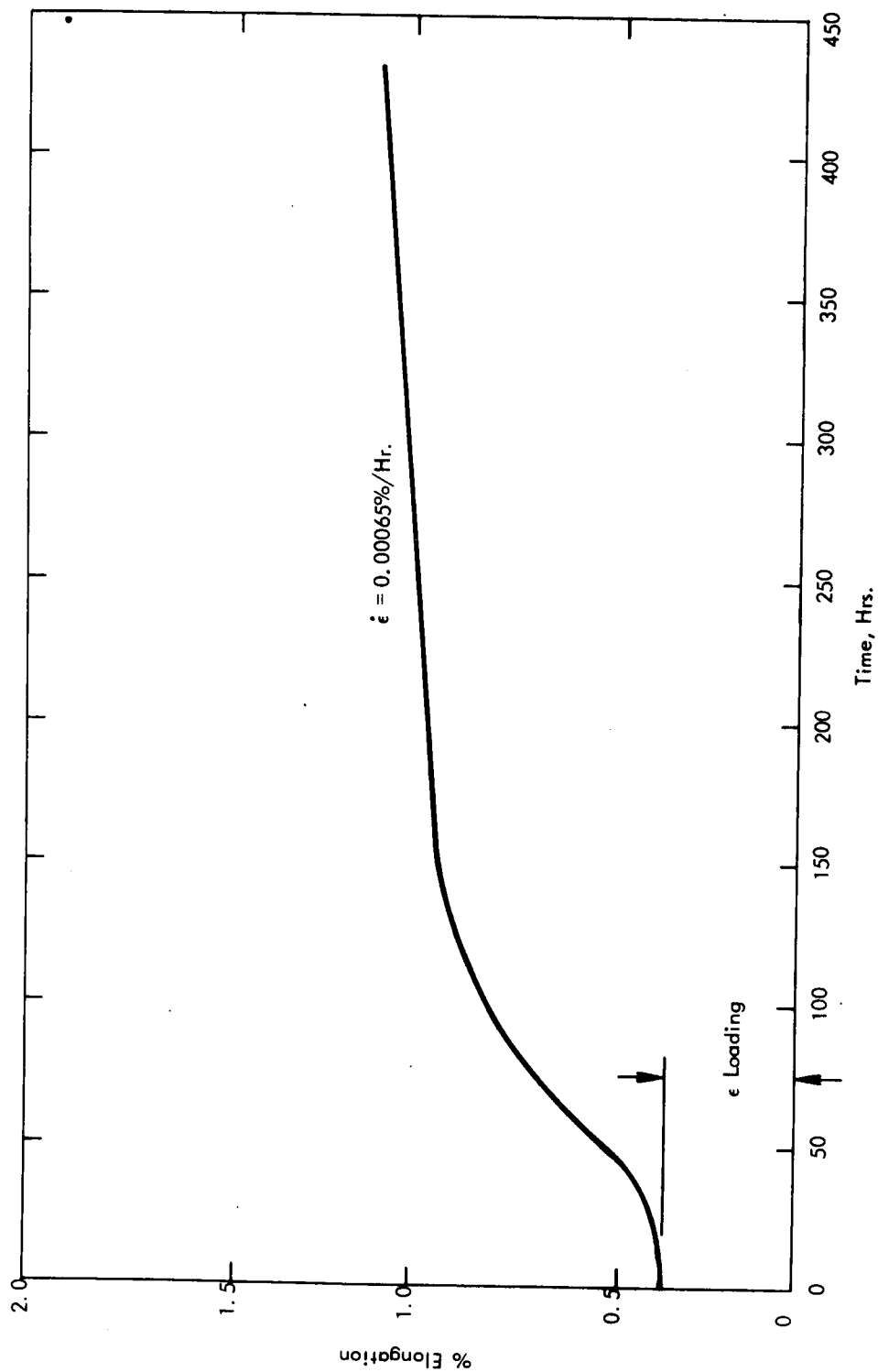
Figure 13. Creep Behavior of Ta-13W-1.5Re-0.7Hf-0.025C at 50,000 psi and 1850°F (Specimen annealed 1 hour at 2000°C prior to test)
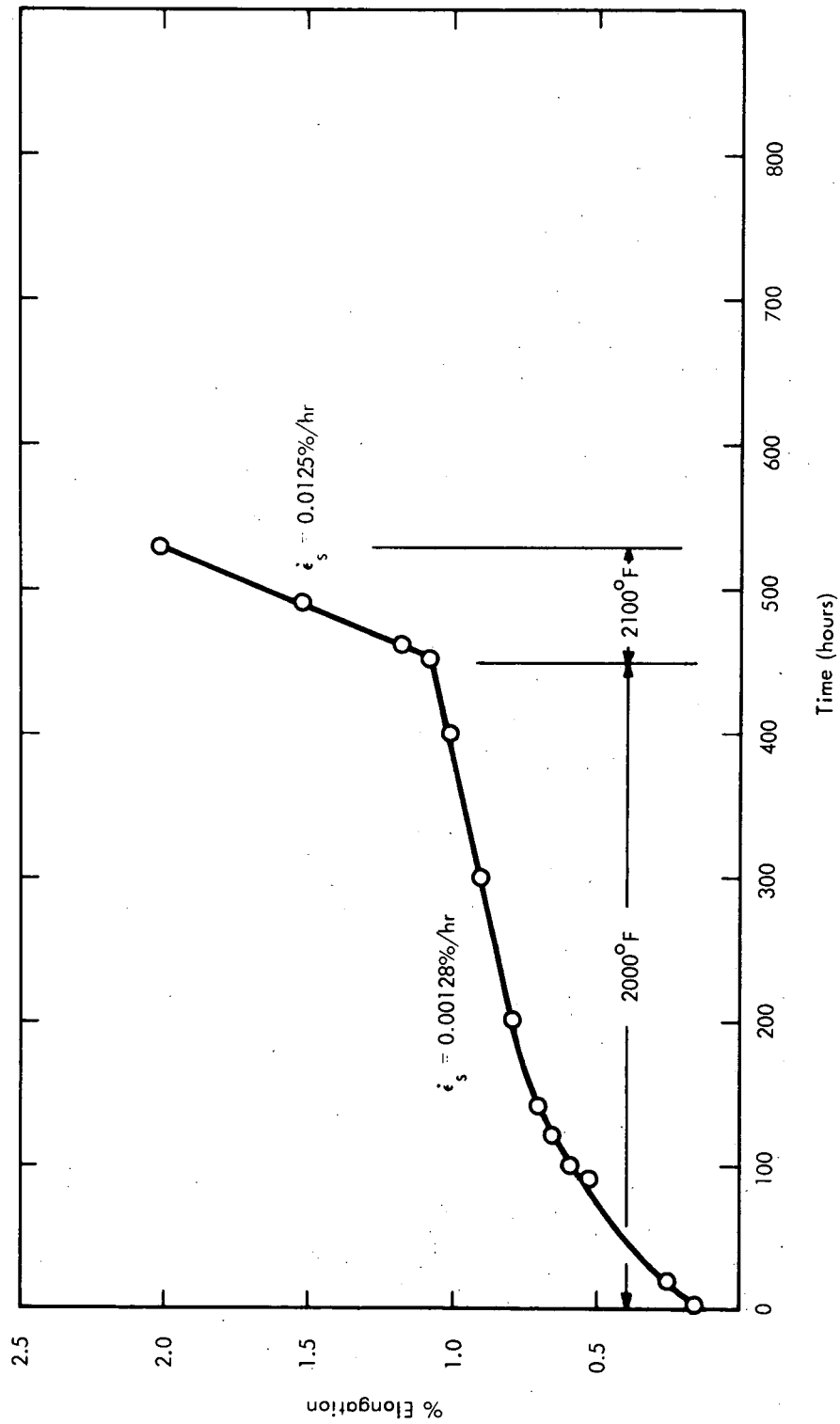
34

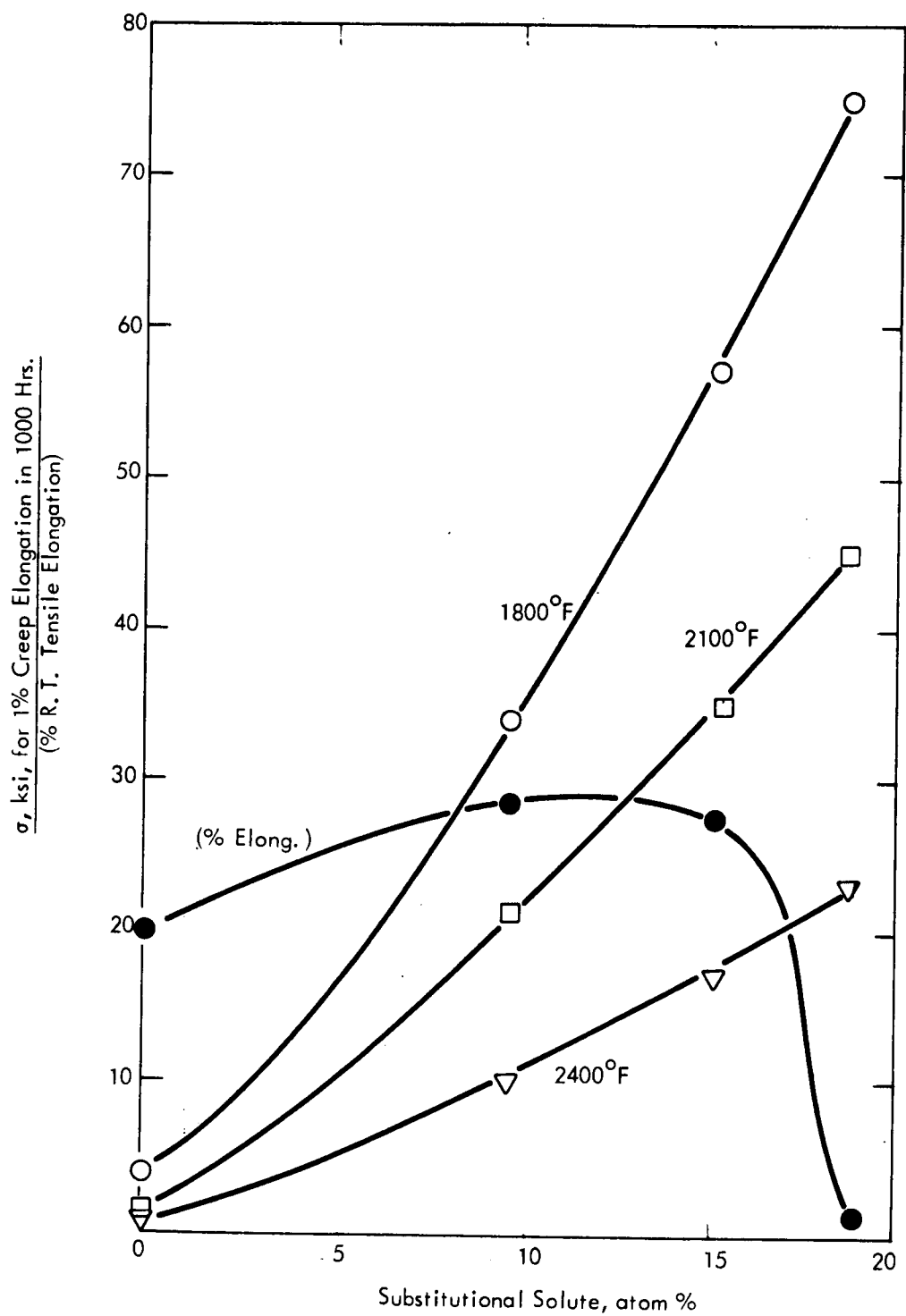Figure 14. Creep Behavior of ASTAR-811C Rod Annealed 1/4 Hour at 3630°F Prior to Test

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Figure 15. Influence of Solute Content (W+Re+Hf) on Creep Properties and Room
Temperature Elongation of Experimental Ta-W-Re-Hf-0.025C Alloys

W+Re. NASVF-4 contained 15W+2Re while NASVF-5 contained 16W+1Re. Examination of the creep data in Table 6 indicates that both alloys are similar and at least at this solute level, the range for rhenium does not appear critical.

Although substitution of nitrogen for carbon did not greatly alter the elevated temperature tensile strength, significant effects were observed on creep properties. The effect of nitrogen substitution for carbon on the creep of tantalum alloy composition is illustrated in Figure 16. At 50,000 psi at temperatures up to 2000°F, the nitrogen bearing alloy has a definite superiority over the carbide counterpart. In addition to extremely low creep rate, loading strain was significantly less and transient creep was not observed as it is with the carbide containing composition. At 2400°F, the nitrogen containing alloy exhibits a superiority initially but this advantage is short lived as the nitride overages and the creep rate increased. As the test temperature was lowered, the nitride strengthened alloy had a higher creep rate (~2X) than that of the carbide bearing composition.

Significant improvement in the creep properties of tantalum base alloys have been achieved by increasing the solute content. A comparison of the creep strength of the experimental tantalum alloy compositions with A-811C, T-111, and the columbium modified TZM alloy is shown in Figure 17. At temperatures above 2200°F, the experimental tantalum base alloys are clearly superior to the Cb modified TZM, even on a density compensated basis.

4.6   Response to Heat Treatment

A carbide strengthened composition, Ta-16W-2Re-0.7Hf-0.025C (NASVF-2), and a nitride strengthened composition, Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3) were subjected to solution annealing and aging treatments to study their response to thermal treatment and the stability of the precipitating phase. Samples 0.25 inch diameter x one inch long were wrapped in tantalum foil and solution annealed at 3600°F for one hour at 1×10^{-5} torr. The specimens were rapidly cooled by introducing helium gas into the furnace chamber. The time from
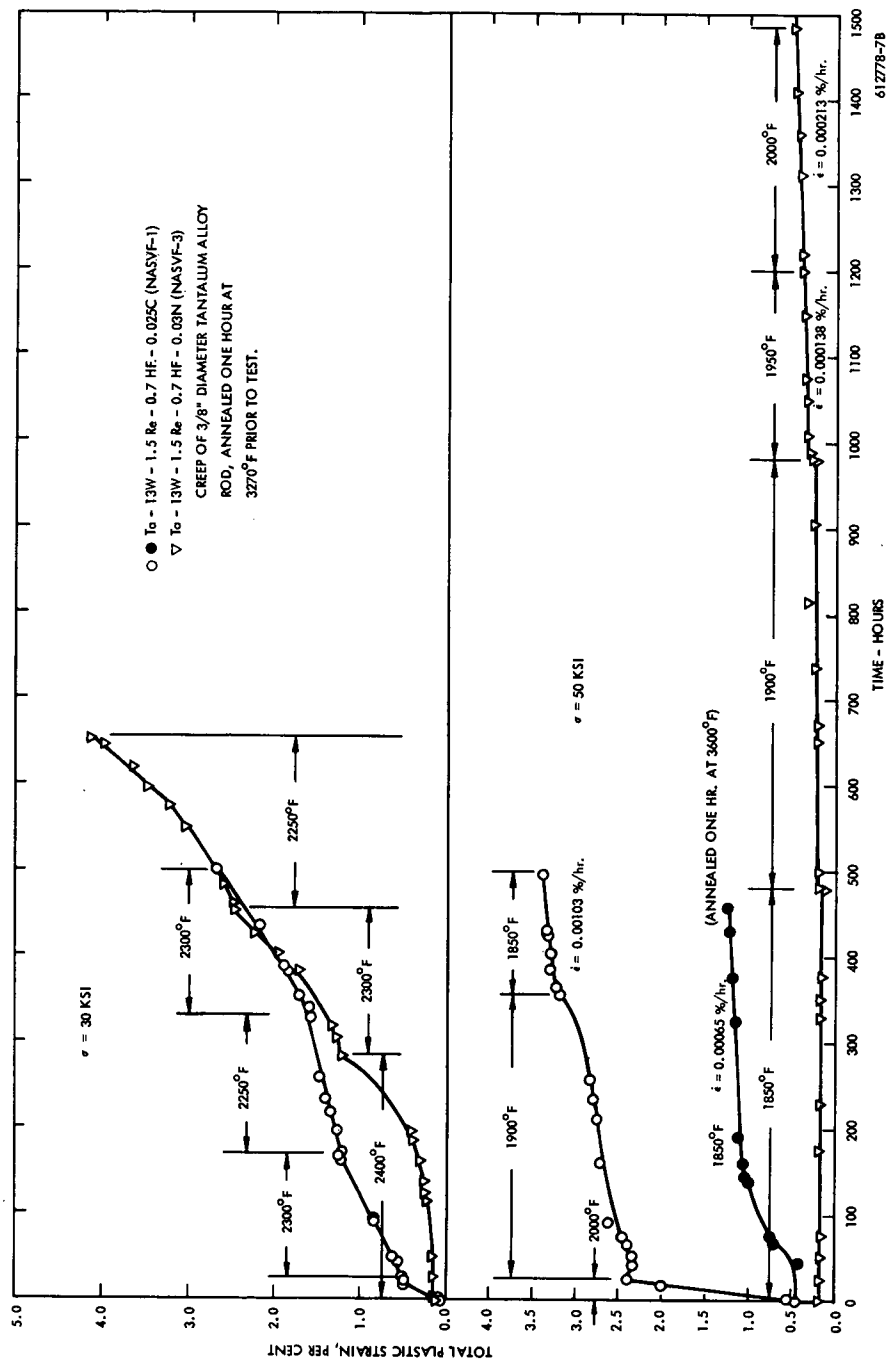
Figure 16. Effect of Nitrogen on Creep Behavior of Ta-13W-1.5Re-0.7Hf-0.025C Alloy
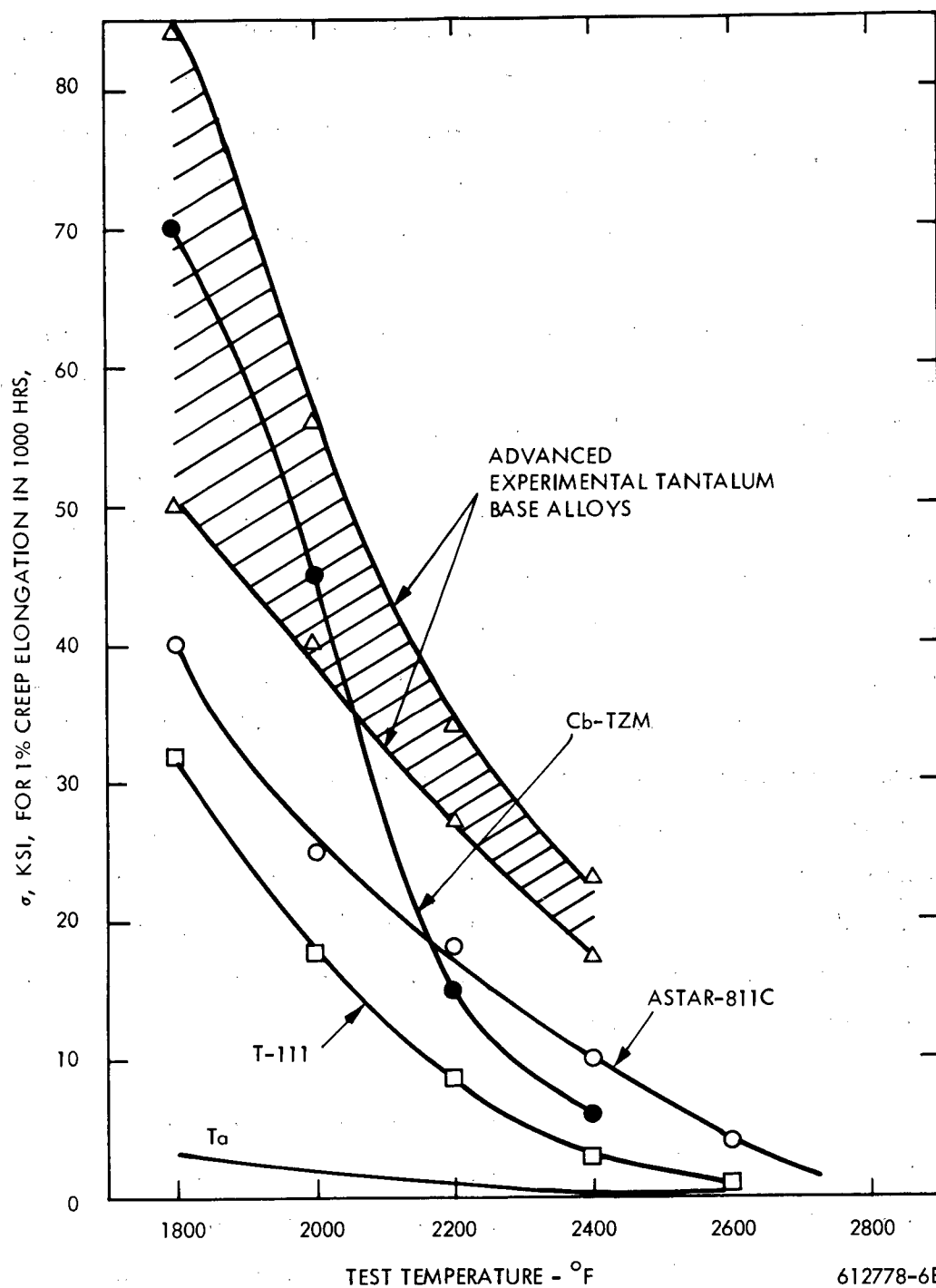
38

Figure 17. Creep Properties of Refractory Metal Alloys

3600°F to black heat required approximately 90 seconds. The solution annealed samples were cut into 1/4 inch thick samples, wrapped in tantalum foil and annealed for 1, 16, 100, and 1000 hours at 1800°F, 2000°F, 2200°F, and 2400°F. The one and sixteen hour anneals were done at 1×10^{-6} torr, in an oil diffusion pumped system while the 100 and 1000 hour exposures were at $\leq 1 \times 10^{-8}$ torr in a sputter ion pumped UHV system.

The room temperature hardness values taken on each of the heat treated samples are tabulated in Table 7 and presented graphically in Figures 18 and 19. The shape of the isothermal hardness curves for the carbide containing composition (See Figure 20) indicate that the solution annealed condition exhibited the highest hardness value and subsequent aging at 1800-2400°F resulted in a hardness decrease. The hardness peak after 1 and 16 hours at 2000°F is not readily explainable since metallographic examination and identification of the chemically extracted precipitates did not give any clue to this behavior. With this exception, the aging response of the carbide containing alloy was similar to that observed for ASTAR-811C and carbide compositions containing nominally 8-10% W+Re with $\leq 1\%$Hf.[1] No apparent correlation between the room temperature hardness and elevated temperature creep properties was observed. Although the hardness at 1800°F had reached a minimum value after approximately 100 hours, there is no indication from the creep curve that there is any metallurgical reaction occurring which is significantly altering the creep strength (See Figure 14). Thus identification of the role of the carbide in promoting elevated temperature creep strength is still unclear.

The nitrogen bearing composition was solution annealed at both 3200°F and 3600°F prior to aging and the response to the subsequent aging treatments was similar for both materials indicating that the nitrogen values for the alloy had been exceeded at the lower solution annealing temperature. As was shown in a previous study,[1] the nitride precipitation kinetics are much more sluggish than for the carbide. The nitride precipitate strengthening follows classical age hardening behavior[1] and the strengthening, both tensile and creep appear to be controlled by the kinetics of the precipitation process. For example, at 2400°F,

Table 7. Room Temperature Hardness of Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)
and Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3) After Solution Annealing
and Aging [a]

Composition-Solution Annealing Treatment/R.A. Hardness	Aging Time (hours)	DPH, Kg/mm^2, After Aging at Indicated Temperature °F			
		1800°F	2000°F	2200°F	2400°F
NASVF-2 1 hour at 3600°F/ 427DPH	1	363	401	358	339
	16	348	376	333	336
	100	349	325	323	330
	1000	318	325	329	328
NASVF-3 1 hour at 3600°F 408DPH	1	386	388	388	414
	16	415	412	410	405
	100	422	375	386	361
	1000	445	346	336	314
NASVF-3 1 hour at 3200°F 394DPH	1	402	413	408	407
	16	405	401	406	406
	100	393	381	385	359
	1000	438	371	337	317

(a) Solution Annealing, one and sixteen hour aging treatment as $\leq 1 \times 10^{-5}$ torr;
100 and 1000 hour aging treatments at $\leq 1 \times 10^{-8}$ torr.
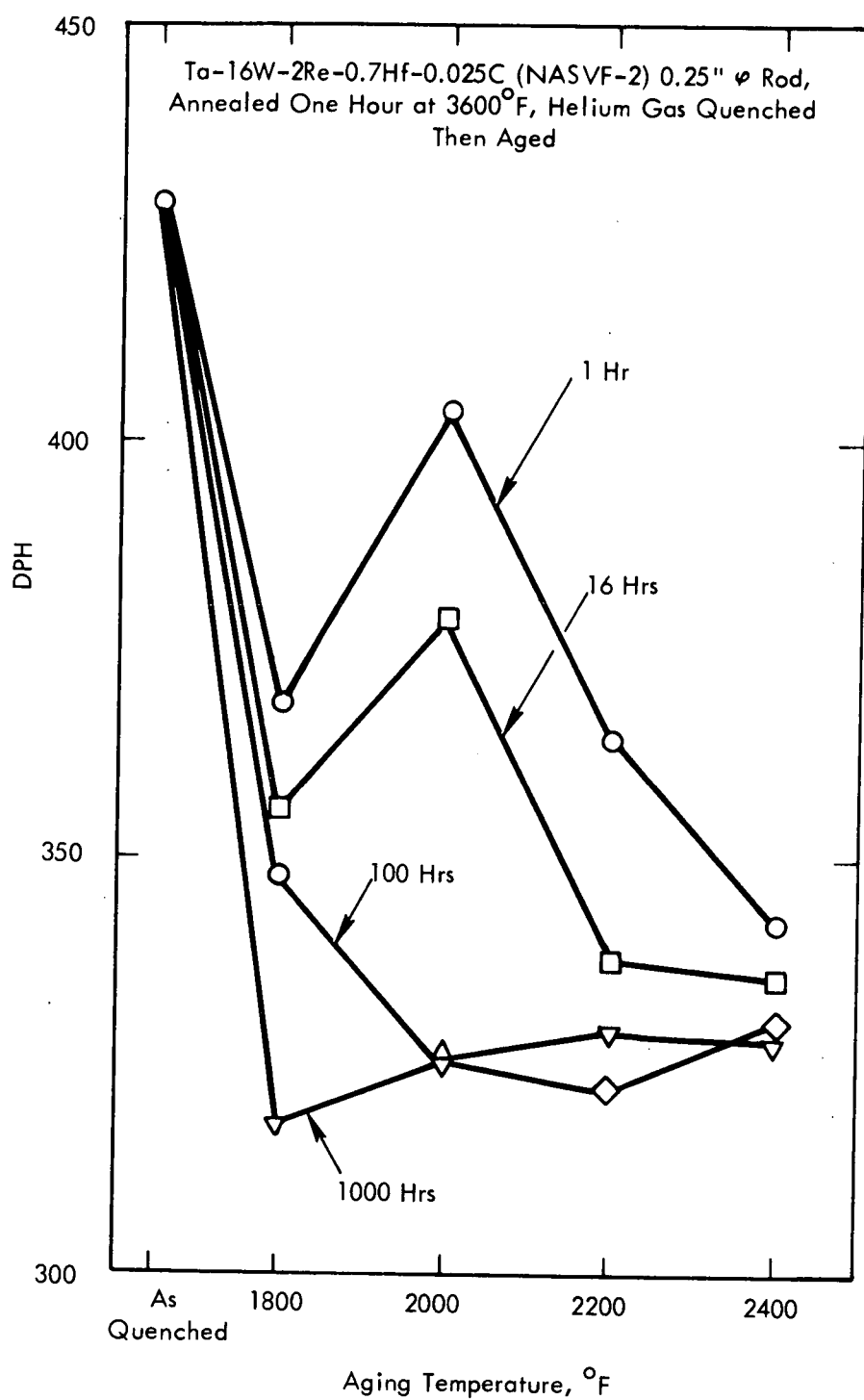
Figure 18. Aging Response of Experimental Tantalum Base Alloy
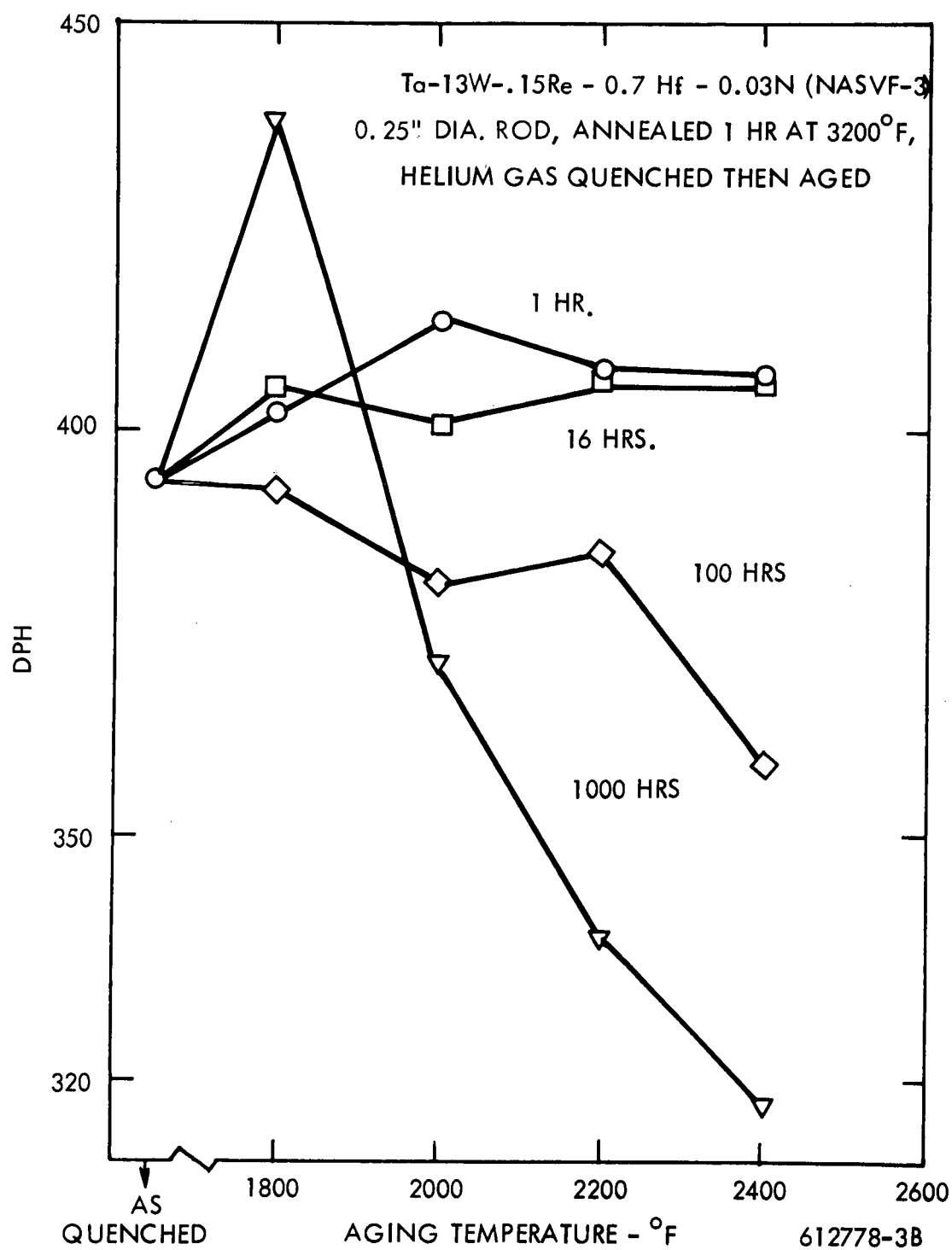
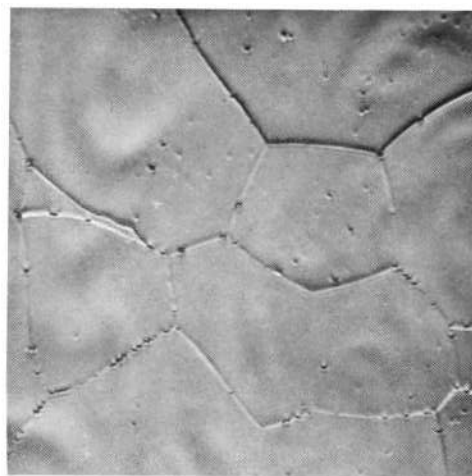Figure 19. Aging Response of Experimental Tantalum Base Alloy

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c) 1 hr at 2400°F 407DPH

f) 100 hrs at 1800°F 393DPH

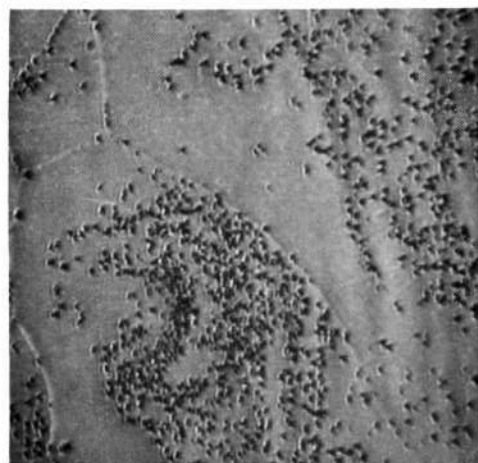b) 1 hr at 1800°F 402DPH

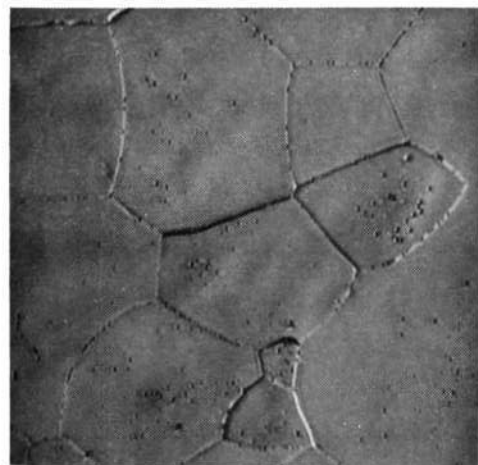e) 16 hrs at 2400°F 406DPH
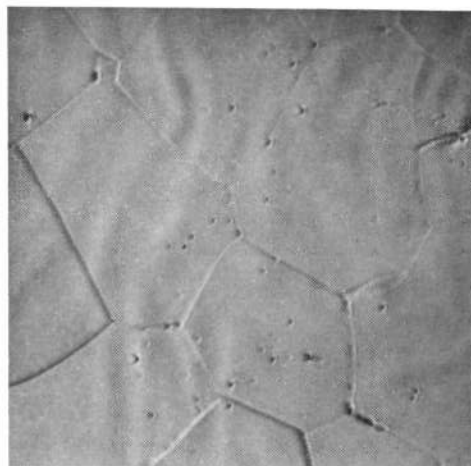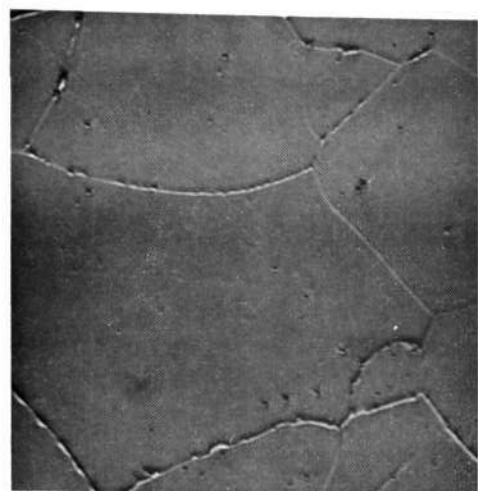
a) As Solution Annealed 394DPH

d) 16 hrs at 1800°F 405DPH

Figure 20. Microstructure and Hardness of Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3) Rod. Solution Annealed 1 hour at 3200°F and Aged as Indicated.
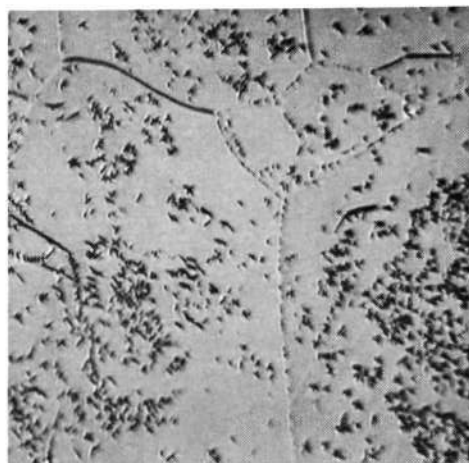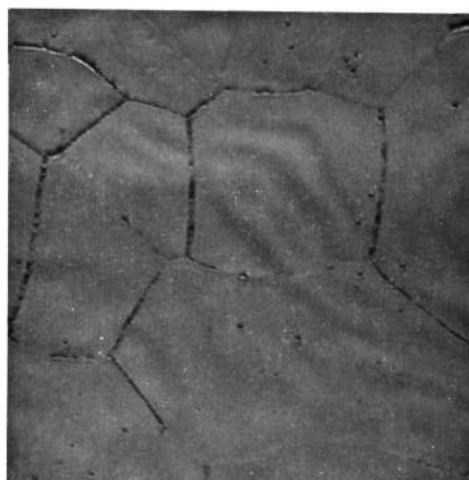
44

i) 100 hrs at 2400°F 359DPH

l) 1000 hrs at 2200°F 337DPH

h) 100 hrs at 2200°F 385DPH

k) 1000 hrs at 2000°F 371DPH

g) 100 hrs at 2000°F 381DPH

j) 1000 hrs at 1800°F 438DPH

Figure 20. Microstructure and Hardness of Ta–13W–1.5Re–0.7Hf–0.03N (NASVF–3) Rod. Solution Annealed 1 hour at 3200°F and Aged as Indicated. (continued)

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overaging of the nitride precipitate occurs in a relatively short time (100 hours): Examination of the creep curve in Figure 16 shows that there is an increase in creep rate occurring with overaging. The overaged non-coherent nitride precipitates are not as effective a strengthener as the carbide upon reduction of the test temperature as also shown in Figure 16.

Metallographic examination of the solutioned annealed and aged samples of NASVF-3 revealed that the solution annealed specimens were single phase when viewed at 1500X. The micro-structures of the heat treated nitride strengthened composition NASVF-3 are shown in Figure 20. They were essentially single phase after aging for times up to 100 hours at temperatures up to 2200°F and corresponded to room temperature hardness values of approximately 380DPH and above. This would indicate that the HfN precipitate is submicroscopic and coherent with the lattice and agrees with prior reported work[1]. The optically resolvable precipitates appear coincident with a drop in hardness below 360DPH.

As noted earlier, there is generally a decrease in hardness as the solution annealed carbon containing composition, Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) was exposed over the temperature range of 1800-2400°F and conforms to the behavior exhibited by ASTAR-811C[1]. The exception being the hardness peak at 1 and 16 hours at 2000°F. The microstructure of the NASVF-2 after solution annealing was essentially single phase when viewed optically at 1500X (See Figure 21a). There was however significant morphological changes in the precipitate occurring after the various time-temperature exposures (See Figure 21). The precipitate was chemically extracted using a bromine-tartaric-methanol solution and the residues were analyzed by x-ray diffraction. For each specimen examined, the dimetal tantalum carbide was found and agrees with phase identification work reported under contract NAS 3-2542. (See Table 8).
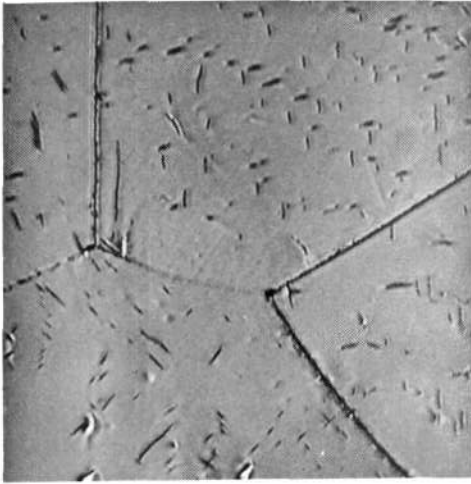
The instability exhibited by the carbide precipitate would tend to indicate that it should not be useful as a creep strengthener. However, as noted earlier, the creep curve at 1800-2000°F for carbide containing compositions did not show any perturbations indicative of metallurgical
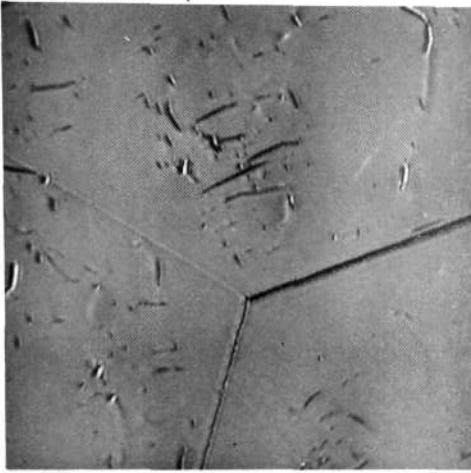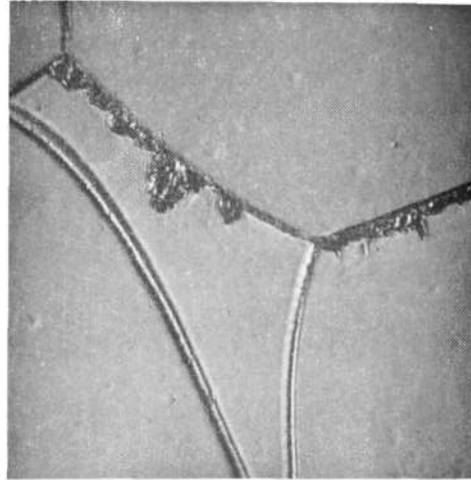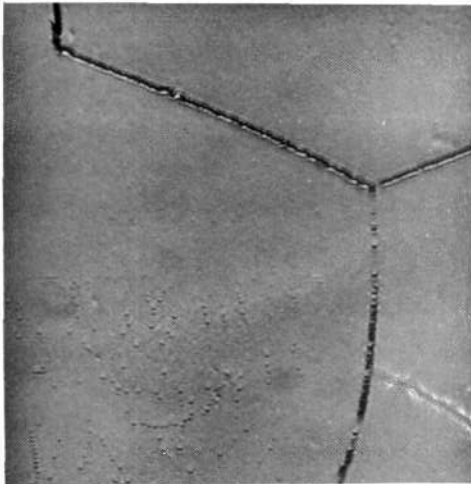
c) 1 hr at 2000°F   401DPH
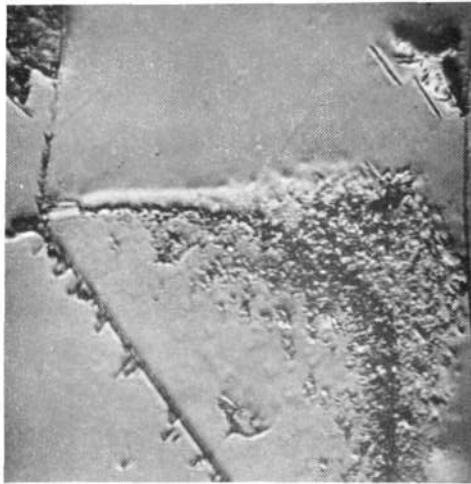
f) 16 hr at 1800°F   348DPH

b) 1 hr at 1800°F   363DPH
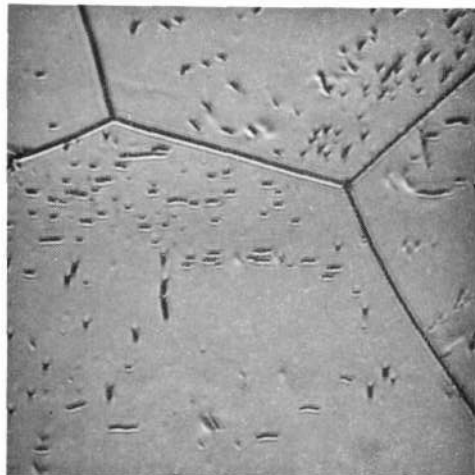
e) 1 hr at 2400°F   339DPH

a) As Solution Annealed   427DPH

d) 1 hr at 2200°F   358DPH

Figure 21. Microstructure and Hardness of Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) After Solution
Annealing at 3600°F for 1 hour and Aging as Indicated.

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g) 16 hr at 2000°F   376DPH

h) 16 hr at 2200°F   333DPH

i) 16 hr at 2400°F   336DPH

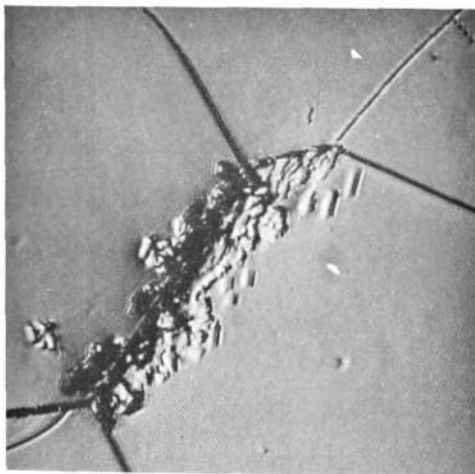j) 100 hrs at 1800°F   349DPH

k) 100 hrs 2000°F   325DPH
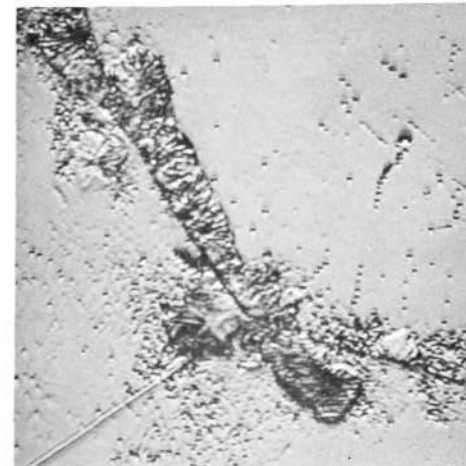
l) 100 hrs at 2200°F   323DPH

Figure 21.   Microstructure and Hardness of Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) After Solution Annealing at 3600°F for 1 hour and aging as Indicated. (continued)

o) 1000 hrs at 2000°F   325DPH

n) 1000 hrs at 1800°F   318DPH

m) 100 hrs at 2400°F   330DPH
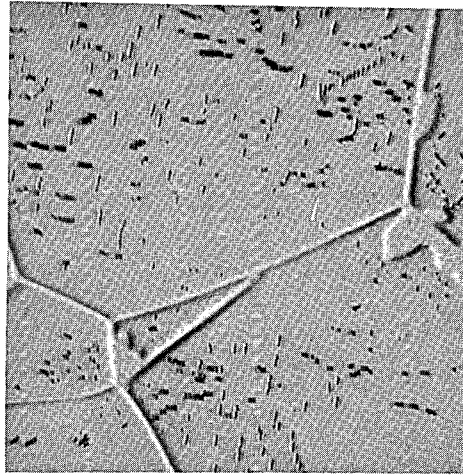
q) 1000 hrs at 2400°F   328DPH
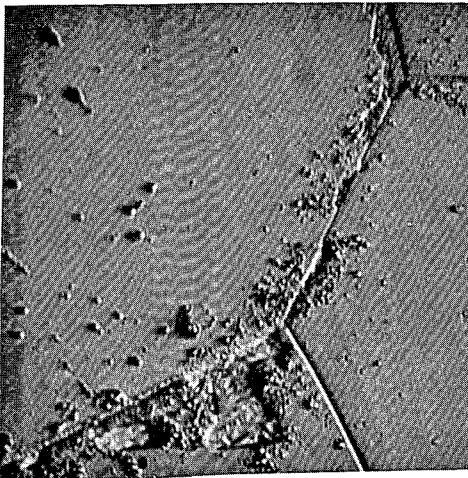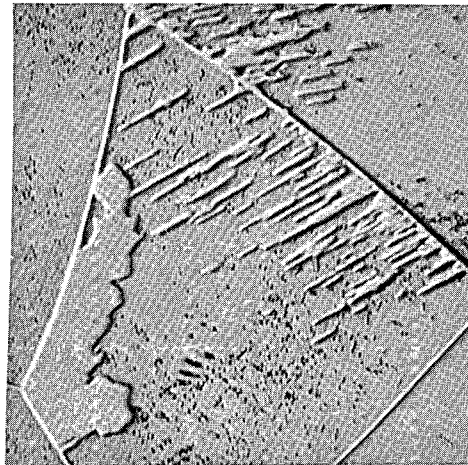
p) 1000 hrs at 2200°F   329DPH
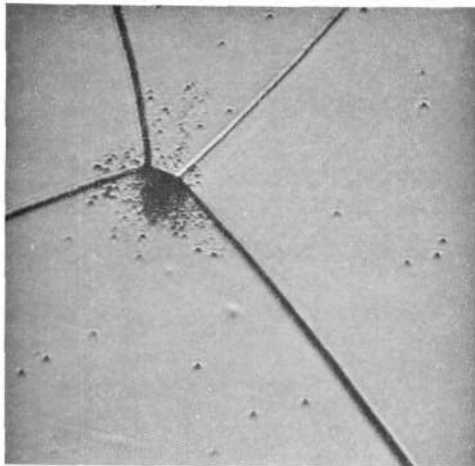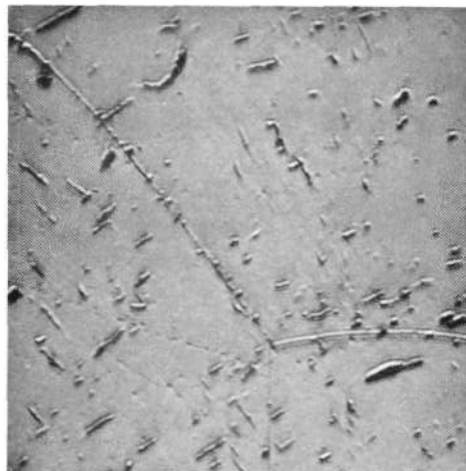
Figure 21.   Microstructure and Hardness of Ta–16W–2Re–0.7Hf–0.025C (NASVF–2) After Solution
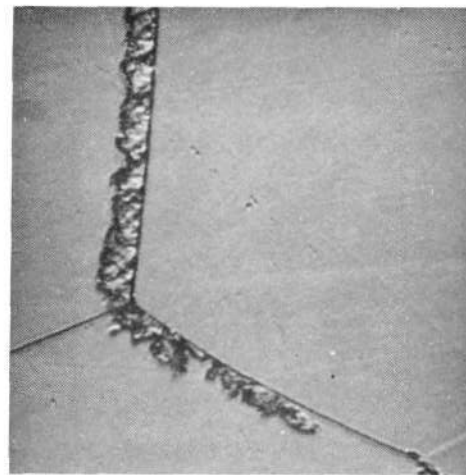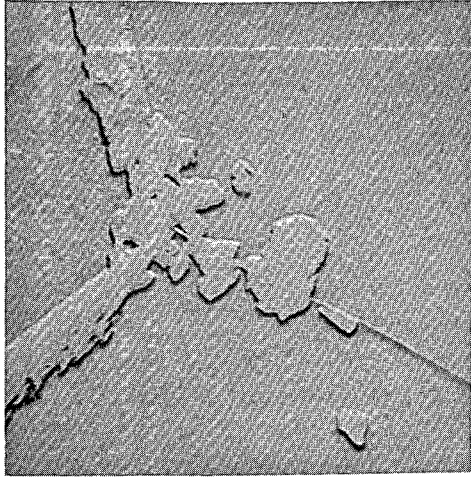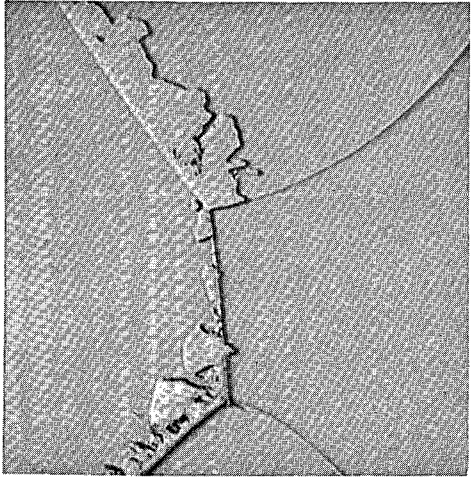Annealing at 3600°F for 1 hour and Aging as Indicated. (continued)

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Table 8. Effect of Thermal Treatment on Composition of Precipitate in Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)

Prior Treatment	X-Ray Identification of Precipitate [*]
1) 1 hr at 3600°F	Ta_2C
2) (1) + 1 hr at 1800°F	Ta_2C
3) (1) + 1 hr at 2000°F	Ta_2C
4) (1) + 1 hr at 2200°F	Ta_2C
5) (1) + 1 hr at 2400°F	Ta_2C
6) (1) + 16 hr at 2000°F	Ta_2C
7) (1) + 100 hr at 2000°F	Ta_2C
8) (1) + 1000 hr at 2000°F	Ta_2C
9) (1) + 1000 hr at 2400°F	Ta_2C

[*] Powder residues exposed in a Siemens 114mm camera Cu K_α radiation

a_o = 3.107 Å

C_o = 4.944 Å

C/A = 1.591

the effectiveness of carbon in improving creep strength has been demonstrated.[1]

To evaluate the effect of the prior thermal history, room temperature tensile properties were determined on specimens that had been creep tested and the data are in Table 9. With the exception of the ASTAR-811C, significant reductions in tensile strength and elongation were observed. Since during elevated temperature exposure carbide precipitation results in a decrease in room temperature hardness, a reduction in room temperature tensile strength would be expected. However, the reduction in tensile elongation for the Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1) was not expected. The post creep test microstructure of the Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1), Ta-16W-2Re-0.7Hf-0.025C (NASVF-2) and ASTAR-811C (Ta-8W-1Re-0.7Hf-0.025C) were similar and the typical microstructure is shown in Figure 22. The microstructure shown is for specimens tested over the temperature range of 1850-2100°F and consists of a relatively clean matrix with massive carbide precipitates at grain boundaries. The same precipitate morphology was observed for ASTAR-811C, however, the room temperature tensile elongation of ASTAR-811C was virtually unaffected by the prior creep history. (See Table 9). Examination of the brittle fractures showed them to be mixed with fractures occurring by a combination of transgranular cleavage as well as along the grain boundary carbide phase (See Figure 23). The reason for the reduction in tensile ductility for NASVF-1 may have been caused by damage during creep testing; (i.e. formation of voids or cavities) however, none were observed metallographically at 1500X. This mode of damage was observed for the nitride strengthened composition NASVF-3 and readily explains the strength and ductility changes for NASVF-3 creep tested at 2400-2200°F prior to room tensile testing (See Table 9). The NASVF-3 specimen tested at 1850-2000°F showed that aging occurred during creep testing since the hardness increased from 399DPH as annealed to 449DPH during creep testing and the ductility and strength change most likely occurred as a result of an upward shift in the ductile to brittle transition temperature.

Table 9. Room Tensile Strength of Carbide and Nitride Strengthened Tantalum Base Alloys After Creep Testing

Composition	Thermal Treatment	0.2% Offset Yield Strength psi	U.T.S. psi	% Elong. Unit	% Elong. Total	Hardness DPH
Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1)	1 hr at 3270°F	118,600	139,900	14.3	28	346
	1 hr at 3270°F + 25 hrs at 2400°F + 142 hrs at 2300°F + 163 hrs at 2250°F total creep strain 2.68%	105,900	106,800	0.5	0.5	299
	1 hr at 3270°F + 25 hrs at 2000°F + 329 hrs at 1900°F + 144 hrs at 1850°F + 1 hr at 3630°F + 430 hrs at 1850°F total creep strain 4.60%	113,000	113,000	0.9	0.9	290
Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)	1 hr at 3270°F	170,000	172,000	1.8	1.8	410
	1 hr at 3630°F + 160 hrs at 1850°F + 144 hrs at 1900°F + 170 hrs at 1950°F + 228 hrs at 2000°F + 298 hrs at 2050°F total creep strain 1.34%	82,600	82,600	0	0	328
	1 hr at 3630°F + 364 hrs at 2400°F + 258 hrs at 2350°F total creep strain 2.03%	117,000	117,600	.3	.3	338
Ta-8W-1Re-0.7Hf-0.025C (NASV-20) ASTAR-811C	1 hr at 3630°F	90,000	105,000	15	22	262
	1 hr at 3630°F + hrs at 2000°F + hrs at 2100°F + hrs at 2000°F total creep strain 2.50%	78,300	90,700		18.8	231
Ta-13W-1.5Re-0.7Hf-0.03N (NASVF-3)	1 hr at 3270°F	160,000	166,000	15.7	16	399
	1 hr at 3270°F + 500 hrs at 1850°F + 480 hrs at 1900 + 22 hrs at 1950°F + 292 hrs at 2000°F total creep strain .48%	154,500	154,500	0	0	449
	1 hr at 3270°F + 290 hrs at 2400°F + 170 hrs at 2300°F + 165 hrs at 2250°F total creep strain 3.72%	100,400	100,400	0.1	0.1	357
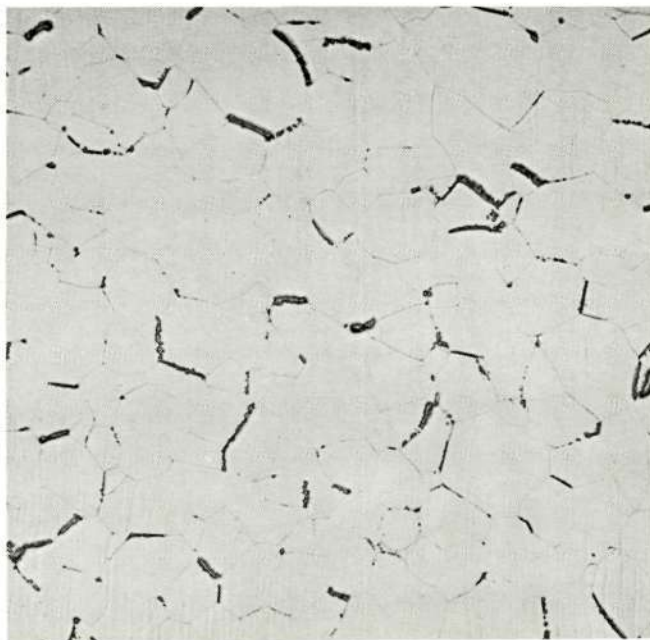
100X

Figure 22. Microstructure Representative of Post Creep Tested NASVF-1,
NASVF-2 and ASTAR-811C
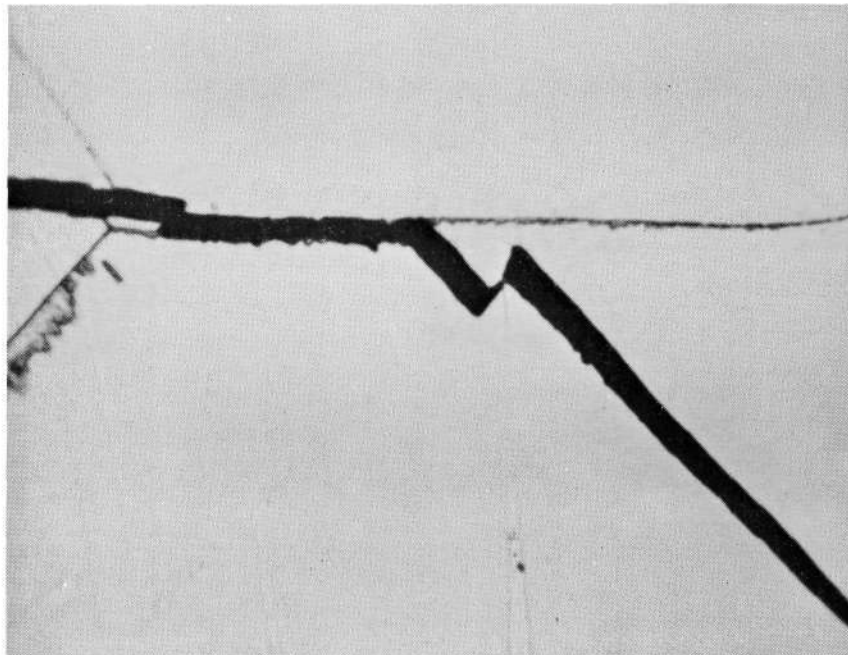
1500X

Figure 23. Photomicrograph Near Room Temperature Tensile Fracture Showing
Crack Propagation by Transgranular Cleavage and Along Grain
Boundary Carbide Precipitate for Ta-13W-1.5Re-0.7Hf-0.025C
(Specimen NASVF-18-1C See Table 9 for Prior Thermal Strain History)

4.7 Chemistry Stability

The carbon content of selected samples was determined to evaluate any chemistry change resulting from the various thermal treatments. Decarburization has been shown to occur for ASTAR-811C sheet, 0.035 inch thick when exposed to temperatures above 3400°F at pressure of nominally 1×10^{-5} torr. All of the round bar specimens analyzed did not show any significant change in carbon (See Table 10) as a result of the various thermal treatments. Since decarburization occurs by methane and CO reaction, and is controlled by the rate of arrival of reactants to the surface, it would be expected that the rate of decarburization would be less for round bar than for thin sheet since the sheet would have a much greater surface area to volume ratio.

4.8 Weldability

ASTAR-811C (Ta-8W-1Re-0.7Hf-0.025C) exhibits good GTA weld ductility coupled with good creep strength. Although the advanced experimental alloy compositions were designed to increase strength at elevated temperature, moderate ductility was exhibited by electron beam welded Ta-13W-1.5Re-0.7Hf-0.025C alloy (NASVF-1). A 0.25 inch diameter rod was annealed one hour at 3270°F and a circumferential weld was made. Parameters were selected to achieve penetration to the center of the rod. Specimens were then bend tested at room temperature. In the as electron beam welded condition, brittle fracture occurred upon bending. However, after annealing for one hour at 3270°F, a ductile bend could be made (See Figure 24). The weld ductility is quite remarkable in view of the fact that the alloy contains 14.5 atom percent W+Re in addition to the hafnium and carbon.

Table 10. Carbon Content of Carbon Containing Alloys Solution Annealed at 3630°F for 1 Hour and then Thermally Exposed for Times up to 1000 Hours at Temperatures up to 2400°F [a]

Composition	Specimen Configuration and History	Carbon Content (%)
(1) Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1)	Creep specimen – 0.1 inch dia. gage; annealed 1 hour at 3270°F at 1×10^{-5} torr, creep tested for 500 hours at 1850-2100°F at $<1 \times 10^{-8}$ torr. Re-annealed 1 hour at 3630°F at 1×10^{-5} torr then creep tested additional 460 hours at 1850°F at $<1 \times 10^{-8}$ torr.	0.023[b]
(2) Ta-16W-2Re-0.7Hf-0.025C (NASVF-2)	Creep specimen – 0.1 inch dia. gage; annealed 1 hour at 3630°F at 1×10^{-5} torr, creep tested at 1850-2100°F for 1000 hours at $<1 \times 10^{-8}$ torr.	0.023[b]
(3) NASVF-2	0.3 inch dia. x 1/2 inch long rod, annealed 1 hour at 3600°F at 1×10^{-5}	0.026
(4) NASVF-2	Same as (3) plus 1 hour at 2400°F at 1×10^{-5} torr.	0.020
(5) NASVF-2	Same as (3) plus 1000 hours at 2400°F at $<1 \times 10^{-8}$ torr.	0.025

(a) All samples annealed at 1×10^{-5} torr wrapped with single layer of 0.002 inch thick tantalum foil and cooled from annealing temperature by backfilling vacuum chamber with high purity helium gas containing less than 5 ppm total active impurities.

(b) Carbon content in NASVF-1, Ingot Analysis – 0.024%
    Carbon content in NASVF-2, Ingot Analysis – 0.024%

A. As EB Welded

B. As EB Welded Plus 1 Hr. at 3270°F (1800°C)

|← 1 inch →|

Figure 24. Results of Bend Testing Electron Beam Welded
Ta-13W-1.5Re-0.7Hf-0.025C (NASVF-1) Rod

5.0 CONCLUSIONS

Based on the results of this screening investigation, three alloy compositions were selected for scale-up which should have a good combination of high temperature strength and low temperature ductility. Two of the compositions are carbide containing and are Ta-14W-1Re-0.7Hf-0.025C and Ta-16W-1Re-0.7Hf-0.025C. The third composition, Ta-14W-1.5Re-0.7Hf-0.015C-0.015N was selected to take advantage of the nitride precipitation kinetics which were shown in previous work under Contract NAS 3-2542 to enhance high temperature creep strength. These three alloys will be melted and evaluated as two inch diameter ingot and the results will be the topic of a separate report.

Additional conclusions which were drawn from the results of the screening investigation on the development of high strength tantalum base alloys include the following.

1) The tensile and creep strength of a Ta-1Re-0.7Hf-0.025C matrix increases monotonically with increasing tungsten content over the range of 8 to 16 atom percent tungsten.

2) Room temperature ductility decreases significantly as the total solute (W+Re) exceed 16-17 atom percent.

3) Pronounced morphological changes occurred in the Ta_2C precipitate during aging over the temperature range of 1800-2400°F of solution annealed material. These changes could not be related to creep behavior.

4) The role of the carbide precipitate in enhancing high temperature creep strength was not explainable.

5) Electron beam welded joints of a Ta-13W-1.5Re-0.7Hf-0.25C alloy exhibited room temperature bend ductility after post weld annealing for one hour at 3270°F.

6.0   REFERENCES

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2)   J. C. Sawyer and E. A. Steigerwald, "Generation of Long Time Creep Data on Refractory Alloys at Elevated Temperature," Final Report No. ER-7203, TRW Inc. Cleveland, Ohio, June 6, 1967.

3)   R. W. Buckman, Jr. and R. C. Goodspeed, "Considerations in Development of Tantalum Base Alloys," from Refractory Metal Alloys Metallurgy and Technology, Editors J. Machlin, R. T. Begley, and E. D. Weisert, Plenum Press, New York, 1968.

4)   R. W. Buckman, Jr. and J. J. Hetherington, "Apparatus for Determining Creep Behavior Under Conditions of Ultra High Vacuum," Review of Scientific Instruments, Vol. 37, No. 8, pp. 999-1003, August 1966.

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6)   F. Garofalo, "Fundamentals of Creep and Creep-Rupture in Metals," MacMillan Series in Materials Science